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TRANSACTIONS.

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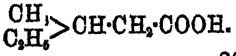
XXXIII.—ββ-Methylethylpropionic acid, 

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JOURNAL

OF

THE CHEMICAL SOCIETY.

TRANSACTIONS.

I.—*A New Method of Determining the Freezing-points of very Dilute Solutions.*

By Percy Benedict Lewis.

Introductory Note by M. Wildermann.—Percy Benedict Lewis, who died on the 29th of March, 1894, at the early age of 23, had been for some time engaged in the investigation of a subject of importance from the point of view of physics, of practical value in organic chemistry, and of great importance in physical chemistry, namely, the best means of determining the freezing points of very dilute solutions. At his request, I have thoroughly tested and verified his method, and the results of his work are communicated in the following paper. Although valuable investigations on the same subject have been already made by Jones (*Zeit. physik. Chem.*, **11**, 110) and by Loomis (Wied., *Ann.*, **51**) Lewis' work is distinguished by greater experimental accuracy, and by the minute and judicious care with which the conditions necessary to secure the best possible results are investigated.

It was his wish that his thanks should be given to the authorities of Christ Church, and to Mr. A. G. Vernon Harcourt, for placing the resources of their laboratory at his disposal.

I have applied the method described to the more exact investigation of Arrhenius' law as to the connection between the depression of the freezing point and the electrical conductivity; of Van't Hoff's constant; and of Ostwald's law of dilution, forming, as they do, the foundation of modern theories of solution. For this purpose very dilute, aqueous solutions of phosphoric acid, cane sugar, phenol, urea, ethyl alcohol, dichloracetic acid, trichloracetic acid, and orthonitrobenzoic acid were chosen; the agreement between the theory and the experimental results surpassing my expectations. The results thus far obtained will form the subject of a separate communication, and I intend to continue the investigation, and also to examine by the freezing point method cases in which the dissociation values for a mixture are affected by the presence of a common ion.—[M. W.]

The Method Employed.

The thermometer A, Fig. 1, used for delicate measurements was of Beckmann's form, and was graduated into thousandths of a degree; the mercury reservoir was 117 mm. long and about 20 mm. in diameter, and the expansion at the top of the capillary tube, *i*, was large enough for the thermometer to be used over a range of temperature from —20° to 30°. The whole scale, whose length was 220 mm., corresponded to 0·58° C. The thermometer was of Jena glass, and was made by the same instrument-maker (Götze, of Leipzig) as the one used by Jones. This thermometer was fixed in a very thick cork *k*, and by its side in the same cork, was a second Beckmann thermometer B, divided into 100ths of a degree, also made by Götze. A piece, *b*, was cut out of the cork (see Fig. 2), after a hole *a*, of a suitable size, had been bored, and the large thermometer with the india-rubber ring *c′* was placed in the hole which was closed again with the piece *b*. The thermometer was thus almost rigidly fixed, so that when the cork was gently tapped it could move only slightly, whilst the mercury in the upper reservoir was but just moved. The small thermometer was merely put through a hole *d*, in the cork, the india-rubber ring *c″* being fastened on it. The vessel which held the solution under investigation was a beaker D, of about 1600 c.c. capacity, and the quantity of solution used for each observation was 1250 c.c. The beaker, which stood in a zinc vessel E to serve as an air-chamber, rested on a mat of thick felt, *l*, which was encased in gutta-percha tissue to keep it dry; the beaker was covered with a glass plate through which the thermometers and a stirrer passed without friction. Between the sides of the beaker and those of the zinc vessel was an air space about 40 mm. wide; the zinc vessel had a cover of the same material in which a round hole was cut, and in this the thick cork with the thermometers was fixed; the stem of the stirrer, C, passed through a third hole, *n*, in the cork.

The stirring of the liquid was effected by means of a double porcelain stirrer, *c*, Figs. 1 and 3, consisting of two porcelain plates 100 mm. in diameter, placed parallel to one another at a distance of 15 mm., and fastened together by four small porcelain rods, and the large rod *a*. In the middle of each of the porcelain plates was an oval hole, *i* (36 mm. broad, and 51 mm. long), so that they could easily pass over both thermometers, and the liquid could be easily and thoroughly stirred without disturbing the thermometers. There were besides eight

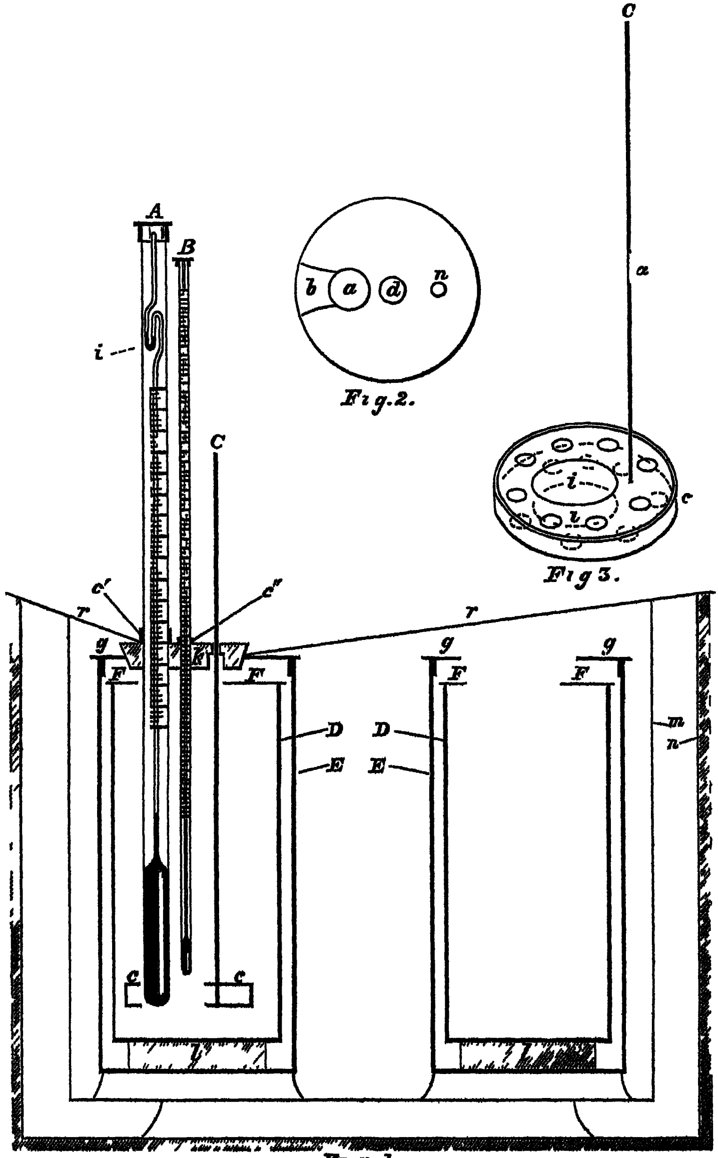

Fig. 2.

Fig 3.

Fig. 1.

circular holes in each plate, so arranged that the holes in the upper one were not immediately over those in the lower; by this arrangement, side currents were caused to flow in all directions through the liquid, so that even when the stirrer was moved but gently at the bottom of the beaker, the liquid was very perceptibly mixed even in the topmost layers. On moving the stirrer up and down, currents are sent in opposite directions. Stirrers of various materials (gutta-percha, heavily gilt copper, &c.) were tried, but the best results were obtained with the porcelain stirrer, especially when dealing with acids and alkalis. We did not try a platinum stirrer, which would have been not only heavy but costly. This porcelain stirrer was specially made for the purpose; but stirrers of the same kind can now be obtained at Messrs. Townson and Mercer's, London.

It was found to be absolutely necessary, not only that the thermometers should be kept continuously at 0° for some months before they were in a condition fit for using in these experiments, but also during the time which elapsed between one experiment and another; for if the thermometer be allowed to remain for several hours at the ordinary temperature of the room, it must be kept at 0° for two or three days before it can be used for another experiment. In order to provide for this, a second zinc vessel, similar to that which held the liquids under observation, was placed in the ice bath, and in it was a beaker containing pure distilled water, partly frozen, and in this the thermometers were kept immersed during the intervals between the experiments; the temperature of this distilled water showed variations of only some hundredths of a degree above or below 0°. When actually experimenting, it is necessary to keep the thermometer for as short a time as possible in the liquid which is cooled below its freezing point; that is to say, that the freezing had to be determined as soon as possible by the introduction of a little fragment of ice. Moreover the mercury was never allowed to enter far into the upper reservoir, so as to insure that it should always recede completely on cooling. The temperature of the cooled solution was always read off directly on the smaller thermometer alone, the scale of which was divided into hundredths of a degree.

Both the zinc vessels, holding respectively the experimental liquid and distilled water, stood in a large zinc vessel, *m*, serving as an ice bath, and this again in a still larger vessel, *n*, with an air space of several centimetres between them; the outer vessel, moreover, stood upon a thick mat of felt, and was also covered with a thick coating of felt. Both the tops of the ice-bath and of the outer vessel were covered with pieces of thick asbestos cardboard, *r r*, up to the central cork.

It will be seen that the object of the whole arrangement is to maintain the temperature of the ice bath for a length of time as constant as possible; the temperature of the bath being adjusted in such a way that the solution to be cooled down is only exposed to exceedingly slow changes of temperature. Direct experiments with a freezing mixture at −2° to −2·3° in the bath, and a temperature of 12—18° in the room, proved that the rate of cooling, when the stirrer is but occasionally and slightly moved, is from 0·013° to 0·017° in five minutes, and when the stirrer is moved continuously but quietly, from 0·0085° to 0·01°. If ice has been already formed in the solution, and is thoroughly mixed with it, the fresh ice, which is formed during the 15—20 minutes of the experiment, will make the solution only about 0·03 or 0·04 per cent. more concentrated—a difference which is immaterial. If, however, the ice cannot be thoroughly mixed with the solution, as happens when the bath is too cold, then even if the temperature of the bath has only sunk to −2·3°, the liquid itself continually cools down, and a constant temperature can no longer be obtained. The above observations and also the experiments made by Loomis (*Ann. Phys. Chem.*, **51**, 519) show that a constant temperature in a mass of liquid may be obtained with greater ease and certainty by means of an air bath than with a liquid bath; for the latter, even if it is only −0·3° below the freezing temperature of the solution, always affects the vessel of liquid placed in it with comparative rapidity.

It was found that if the temperature of the air was from 12° to 18°, the best results were obtained when the temperature of the cooling bath was −1·8° to −2°, but if the temperature of the room rose to 24°, the bath had to be cooled to −2·1° or −2·2°.

The cooling bath is prepared by placing a considerable number of small pieces of ice in water, stirring well, and then adding salt in small quantities until the necessary temperature is obtained; if too much salt be added, this can be corrected by diluting with water; before using the mixture, it should be well stirred until the temperature is the same at different levels. Under these conditions, the variation of temperature in the mixture in the course of two hours will be less than 0·1°. After the bath is in working order, the liquid to be investigated must be cooled below its freezing point at least 0·55° or 0·6° in order that enough ice may be formed on freezing; in a good determination, this super-cooling should lie between −0·7° and −1°, and should be maintained as constant as possible throughout a whole series of determinations, both with water and with the aqueous solutions.

When the above conditions are observed, a satisfactory determination of the freezing point can be obtained; the reading of the thermometer remains constant for 10 to 15 minutes after it has reached its maximum, and the mercury in the thermometer has ample time to acquire the temperature of the liquid.*

It may be further noted that the choice of a beaker for the experiment is of importance; it should be as cylindrical as possible throughout its whole length; if the diameter of the stirrer is 100 mm., the diameter of the beaker should be between 107·5 and 109 mm. If it be as little as 106 mm., it is impossible to get a good determination with certain concentrations of solution, as the ice formed cannot pass freely between the stirring rod and the walls of the beaker, but is pressed into compact masses against the beaker and removed from the solution almost completely, or else it forms a compact mass on the bottom of the beaker. If, on the other hand, the beaker be wider than 109 mm., it becomes difficult to stir the liquid effectually. Before starting on a series of determinations, this point should be carefully ascertained by direct experiment with a few selected beakers.

It is impossible to insist too strongly that neither the constancy of the thermometer reading in one experiment nor the agreement of the thermometer readings in successive experiments, affords in itself a sufficient guarantee that a correct determination of the freezing point has been obtained. It is absolutely necessary to examine the solution at the end of the experiment, and to make sure that it contains a sufficient quantity of finely-divided ice, uniformly distributed, and that there is no accumulation of compact ice either round the thermometer or on the walls of the beaker. This precaution is absolutely necessary, but if the operation be carefully performed, and all the precautions indicated be observed, an unsuccessful experiment will be of rare occurrence.

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* These conditions also bring about a convenient formation of ice in the form of fine flakes distributed uniformly throughout the whole liquid. A curious difference in the mode of separation of ice under different circumstances may here be noticed. In solutions which show a depression of freezing point of about 0·02°, ice almost always forms throughout the liquid, but that is not the case with pure water. With the latter, the ice forms in fine crystals throughout the liquid, but at once aggregates, forming a cap round the bulbs of the thermometers, and settling in a thick layer round the stirrer.

There is no doubt that the correct freezing point can only be obtained when ice is formed in fine flakes throughout the solution; and it is equally certain that it cannot when an ice-cap forms round the bulb of the thermometer. Comparative experiments, in which the formation of an ice-cap was sometimes allowed to take place, and sometimes prevented, gave uniformly lower readings for the freezing point in the former case. From this it will be seen that the agreement of readings in successive experiments is no guarantee that the freezing point observed is the true one. There can be no doubt that a correction must be applied in the determination of the freezing point of water for a constant error due to the formation of an ice-cap round the bulb of the thermometer: the accurate determination of this correction is a matter of great importance, and will form the subject of a later communication.—M. W.

The Two Thermometers (0·01° *and* 0·001°).

In stating the conditions under which an accurate determination of the freezing point of a solution is possible, it has been assumed that a thermometer divided to 1/1000° C. has been used, because with such |a thermometer more delicate and accurate determinations of freezing points can be made than with a thermometer divided only to 1/100° C. Nevertheless, all the experimental precautions described above should be taken in order to obtain a good determination with the 1/100° thermometer; by the use of the more delicate thermometer, the conditions necessary for a successful determination have been more definitely ascertained and controlled. Kohlrausch (*Ann. Phys. Chem.*, 51, 527—528) has recently adduced several *à priori* objections to the use of the more delicate instrument. The best way to judge of the force of his objections is by simultaneous observations with the two thermometers. The description of the precautions required in the execution of the experiment makes it clear to what extent the doubts of Kohlrausch and of Dieterici (*Ann. Phys. Chem.*, 50, 78) are justified.

One difficult question remains to be answered, namely, what is the effect of a variation in the barometric pressure on the reading of the thermometer? Any variation of the actual freezing temperature due to variation of barometric pressure may be neglected.

Before considering this point, however, a question which has been recently brought forward by Kohlrausch must be dealt with. Kohlrausch writes in reference to the freezing point determinations made by H. C. Jones:—"If the glass of the bulb of the 1/1000° thermometer were very thin, the following difficulty must be considered. The thermometer was allowed to remain in the solution even when it was cooled 1·2° below the freezing point. At the moment of solidification the mercury rose in the stem by about 20 cm., so that the increase in the length of the mercury column would cause an increase of pressure of about a quarter of an atmosphere on the inside of the bulb. It is possible that the consequent expansion due to the elasticity of the glass may cause a gradual variation in the reading." Kohlrausch proposes to settle this question by simply inclining the thermometer; but this method would be inapplicable for large variations of pressure, because it is only possible to obtain a definite freezing temperature under very definite conditions and with very special precautions, and in this case, where the effect to be measured is necessarily very small, no conclusions could be drawn from a rough experiment. The thickness of the cork in the apparatus above described made it possible to incline the thermometer to an extent corresponding to a difference of pressure of 10 to 15 mm., but no change in the reading of the thermometer could be detected. Further information on this point was obtained in the course of the investigation of the effect of different degrees of super-cooling on the readings in the case of water. As no variations of concentration can occur in the case of water, the observations on this point can be extended over wider limits than in the case of solutions (*e.g.*, 0·6° to 1·2° or 1·3°). Now, if the wall of the bulb be thin enough for the elastic effect to become obvious, the observed freezing point would depend on the extent of the preceding super-cooling.* In the following observations the thermometer was left for as short a time as possible in the super-cooled liquid.

Super-cooling read off on the 1/100° thermometer.	Freezing point of water read on the 1/1000° thermometer.
0·497°	0·4875°
0·607	0·4875
0·647	0·4873
0 827	0·4873

These results seem to show that the thickness of the glass bulb was sufficient to confine within the customary limits of experimental error (one, two, or three thousandth of a degree) the variations due to the two causes mentioned above, namely, the elastic effect caused by the internal pressure, which was applied only for a very short time, and the contraction due to variations in the amount of supercooling of the liquid examined.

But the case is different if the excess of pressure and the lowering of temperature be allowed to persist for any length of time, in which case the effect on both thermometers was observable. If the 1/1000° thermometer be kept at the temperature of the room for some hours, and afterwards used for a series of freezing point determinations under constant or almost constant atmospheric pressure, the observed freezing point shows a continuous rise in consequence of the gradual contraction of the glass bulb. A similar rise is observed when the atmospheric pressure is gradually increased, so as to diminish the volume of the mercury bulb. In the following experiments, which were performed at various times, the water used was not always the same in each pair of corresponding observations, but the mercury was not allowed to rise into the upper reservoir during any pair of experiments.

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* The capillary tube from 0·58° to the mercury reservoir is about 330 mm., and the difference in the pressure will be about 150 mm.

Atmospheric pressure.	Difference.	Reading of 1/1000° thermometer.	Difference.
749·5 mm. 759·3 „	+9·8 mm.	0·4855(6) 0·4819	+0·0036°
750·2 mm. 756·5 „	+6·3 mm.	0·4832 0·4848	+0·0016°
752·6 mm. 761·3 „	+8·7 mm.	0·4839(40) 0·4865	+0·0026°
752·6 mm 758·8 „	+6·2 mm.	0·4840 0·4859	+0·0019°.
749·0 mm. 758·5 „	+9·2 mm.	0·4830(1) 0·4857(8)	+0·0027(8)

From these observations, it appears that an increase of 1 mm. in the atmospheric pressure acting for some time causes a rise of about 0·0003° in the freezing point as observed on the 1/1000° thermometer. The difference between observations made at the same time with the 1/100° thermometer amounted to 0·004° for a difference of pressure of +9·8 mm., 0·002° for a difference of +6·3 mm. These differences in the readings of the small thermometer include the errors of observation, which may amount to 0·001°, to 0·002° if the pressure remains unaltered.

It was found that the use of a microscope with micrometer scale, such that 10 divisions of the scale corresponded to one division of the thermometer scale, was of very little use, as it was impossible to read the thermometer scale and the mercury meniscus at the same time. It is still uncertain what correction should be applied for an alteration of 1 mm. in atmospheric pressure if the change of pressure affects the mercury bulb for one or two hours only; the question can only be decided by experiments made when the barometric pressure happens to change by several millimetres in the course of a few hours. We might expect the correction to be smaller, as the contraction of the glass vessel due to increase of pressure probably takes place very slowly, just as the apparent rise of temperature in a thermometer placed in a cold mixture of constant temperature takes place very slowly and only reaches a maximum after two or three days.

The best plan of obviating this possible source of error is doubtless to rely only on experiments made under favourable atmospheric conditions. The variation of the barometer pressure in the course of 8 or 10 hours is often under 1 mm. and seldom amounts to more than 2 mm. The exceptional days on which the variations are as much as

3 or 4 mm. are unsuitable for delicate freezing-point determinations, however accurately the corrections required may be examined and studied. The only possible remedy in such a case is to make two or three control determinations of the freezing point of pure water in the course of the day; or only to make determinations of freezing points of the more concentrated solutions.

As to the degree of accuracy attained in these experiments, it may be stated that the variations of the thermometer readings amount to one or two, seldom to three ten-thousandths of a degree. In the case of the small thermometer, the differences amount to one or two thousandths of a degree under similar circumstances. It is thus obvious that under ordinary circumstances, when the barometric variation is not excessive, it is possible to make much more accurate and delicate readings with the 1/1000° thermometer than with the 1/100° thermometer.

Manipulation.

A flask with 1250 c.c. of water is left standing during the night in the zinc vessel which is surrounded by ice, so that on the following morning water at about 0° may be obtained for the experiment. The stirrer should be left all night in the beaker filled with distilled water so as to cleanse it; as the experiment is carried on with dilute solutions, this is quite sufficient unless the beaker is a new one, in which case it should be washed first with sulphuric acid, then with water, and finally steamed.

The first step is to make the ice bath of the right temperature (—1·8° to —2°). The beaker and stirrer are then dried with good filtering paper, 1250 c.c. of water of about 0° is poured into the beaker, and the stirrer placed in the beaker together with a thermometer divided to tenths of a degree. The beaker is then placed in the ice bath and the liquid stirred thoroughly now and then with the stirrer; as soon as the liquid acquires a temperature of +0 2°, the greatest care must be observed in further cooling; the beaker must remain at rest and the liquid be stirred now and then very gently. In this operation the stirrer must never be taken out of the liquid neither must it be allowed to rub against the sides of the beaker, or freezing occurs before the temperature reaches —1·2° or —1·3°. When the temperature of —1·2° is reached, the 1/10° thermometer is laid aside and placed in a beaker with distilled water. The outside of the beaker is now dried with a cloth as quickly and gently as possible, and it is placed on a dry mat of felt in the air chamber, taking care that it is in the right position so that the thermometers may be in their proper places with regard to the stirrer. The zinc vessel must then be closed with its asbestos cover, and the stirrer taken out of the liquid for 30 or 40 seconds, so that no ice flakes may form on it; this precaution is especially necessary if the solutions are very dilute. The thick cork with the delicate thermometer is then fixed in its place in the zinc lid.

The stirrer must be so placed as to move freely up and down without touching the thermometers, and the thermometers must be vertical; after some practice, these adjustments take but little time. Now the stirring should go on very quietly, without interruption, and after a very short interval a reading of the 1/100° thermometer should be taken to ascertain the amount of super-cooling. A little fragment of ice is then brought in by laying it against the stem of the stirrer, and the freezing of the liquid, already cooled below its freezing point, is thus determined. As a rule, freezing begins very soon; it must not be too long delayed or ice will be formed on the thermometer and stirrer, as also in solutions which give a depression of about 0·02°. During the rise of temperature, the stirrer must be quietly and uninterruptedly moved by one hand, while with the other, the thick cork is tapped very gently, so gently that there is no rattling of the opal-glass scale of the thermometer, and that only a slight movement of the mercury in the reservoir is perceptible. This must be done in order that the mercury thread may attain its maximum height as quickly as possible. If this continual tapping be omitted, the thread may remain at rest far below its proper position, and then rise suddenly owing to some accidental shake as the stirrer is moved. Any stronger tapping, for example, with a knife on the head of the thermometer, or with the stirrer on the bulb, must be avoided, as this not infrequently causes a break in the thread of mercury at the neck of the bulb. The chief difficulty is to bring about and observe the rise of the mercury through the last thousandth and ten thousandth of a degree. The maximum has been attained when the mercury thread remains in a fixed position for more than a minute in spite of tapping; this usually occurs about five minutes after the time when the rise of temperature was first observed. The temperature must remain constant for 8 to 10 minutes after the maximum has been reached; during this period, about ten readings may be made, and it is sufficient if the stirrer be used several times without tapping, and the cork tapped several times without stirring, before a reading is taken. In the case of the smaller thermometer, the upper end can be gently tapped with a small knife, without danger of the formation of a vacuous space at the neck of the bulb, or of the separation of the thread of mercury. In reading the thermometer a good ordinary lens may be used; this is more convenient than, and, for a practised eye, quite as serviceable as a microscope with a micrometer scale. Individual readings are of course subject to small variations, amounting to one or two or sometimes three ten-thousandths of a degree (see Tables, pp. 13, 14).

After the readings have been made, the condition of the solution must be carefully examined. The cork with the thermometers must be taken off and the beaker removed to make sure that no cap of ice has formed upon the bulb of the thermometer, or any coating of ice upon the stirrer or beaker, but that the ice consists of fine flakes* and is present in the liquid in sufficient quantity. The greater part of the ice is then melted by placing the beaker in a vessel of water of the temperature of the room, and a certain number of c.c. of the solution is drawn off and the same volume of a solution of known strength is added. The more concentrated solution thus obtained must be warmed at first to +0·7° to +1°, and the beaker containing it is then again brought into the ice bath.

From this point a fresh experiment begins, and must be made with the same precautions as the preceding one. In every experiment, the temperature of the bath and of the room, the height of the barometer, and the condition of the ice round the thermometer must be noted.

Corrections.

After the freezing point of pure water or of the solution under examination has been determined, a definite number of c.c. are removed by means of a pipette, and replaced by the same number of c.c. of a solution of known strength; the strength of the resulting solution is then calculated before the freezing point is determined. In calculating the molecular lowering of the freezing point, we have to consider not the degree of concentration thus calculated, but that which actually exists at the freezing temperature after some of the solvent has separated in the form of ice. It is assumed throughout that the dissolved substance does not separate in the solid form along with the solvent. The calculation of the actual strength at the freezing point is very simple; if the solution be cooled to a temperature n° below the freezing point, then it must rise again through n°, and, in doing this, 1 kilo. of the solution will absorb heat equivalent to n calories; now this heat must be obtained at the expense of that which is developed in the formation of ice, and the amount of ice formed will therefore depend on it. The latent heat of fusion of 1 kilo. of ice is 80 cal., hence $n/80$ kilos. of ice must separate, or, in other words, $n \times 100/80$ per cent. of the solvent must solidify. The strength corresponding to an observed lowering of the freezing point must therefore be greater by $100 \div (100 - 100n/80)$ than before solidification took place. As we have only to deal with a correction applicable to very dilute solutions, we can make the approximation that the specific

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[*] For formation of ice on the thermometer and stirrer, especially in determining the freezing points of water and of very dilute aqueous solutions, see footnote, p. 6.

Potassium Chloride Solutions, 1·214 *normal.*

Condition of experiments.		Readings of 1/1000° thermometer	Time		Readings of 1/100° thermometer.
			Hours.	mins.	
1. Distilled water.					*5·50
Bath −1·8°.		0·4873°	12	18	6·147
Barometer 757 mm.		0·4874	12	23	6·147
Temp. of the room 13·5°.	§	0·4873	12	28	6·147
		0·4873(4)	10 minutes		
1′. Distilled water.					*5·32
Bath −1·8°.		0·4872	1	3	6·147(6)
Barometer 757 mm.		0·4873			
	§	0·4872	1	18	6·147(6)
Temp. of the room 13·7°.		0·4872(3)	15 minutes		
2. { −10 c.c., +10 c.c. KCl sol. (sol. = 0·009711 mol. norm.)					*5·215
		0·4520	1	56	
Bath −1·8°.		0·4521	2	1	
		0·4522	2	7	
Barometer 756·8 mm.	§	0·4520	2	10	
Temp. of the room 13·8°.	‡	0·4521	14 minutes		
					*5·20
2′. Bath −1·8° to −2°.		0·4525	5	18	
Barometer 757 mm.		0·4524			
		0·4523			
Temp. of the room 14°.	§	0·4524	5	27	
	‡	0·4524	9 minutes		
3. { −10 c.c., +10 c.c. KCl sol. (sol. = 0·01934 mol. norm.)					*5·19
		0·4197	6	10	
Bath −1·8° to −2°.	†	0·4196	6	14	
		0·4196	6	16	
Barometer 757 mm.	‡	0·4196	6	20	
Temp. of the room 14°.		0·4196	10 minutes		
					*5·257
3′. Bath −1·8 to −2°.		0·4197	7	0	
Barometer 757 mm.		0·4196	7	5	
Temp. of the room 14°.		0·4197	7	10	
		0·4198			
		0·4197			
	†	0·4197	7	15	
	‡	0·4197	15 minutes		

For *, †, ‡, §, see footnotes on next page.

Potassium Chloride Solutions, 1·214 *normal*—(continued).

Condition of experiments.	Readings of 1/1000° thermometer.	Time. Hours.	mins.	Readings of 1/100° thermometer.
4. { −20 c.c., + 20 c.c. KCl sol.	0·3517	8	3	*5·20
(sol. = 0·03845 mol. norm.)	0·3516	8	5	
Bath −1·8 to −2°.	0·3517	8	6	
Barometer 756·8 mm. †	0·3516	8	9	
	0·3517	8	10	
Temp. of the room 14°. ‡	0·3516(7)	7 minutes		
1‴. Distilled water.	0·4876	5	20	*5·31
Bath −1·8°. §	0·4877	5	23	
Barometer 757 mm.	0·4877	5	25	
Temp. of the room 14°.	0·4876	5	28	
	0·4877	5	30	
	0·4876(7)	10 minutes		
4′. { −10 c.c., + 10 c.c.; −10 c.c + 10 c.c.; −20 c.c.	0·3527	6	13	*5·22
{ + 20 c.c. KCl sol. (sol. 0·03845 mol. norm.) †	0·3527	6	14	
Bath −1·8°.	0·3526	6	15	
	0·3527			
‡	0·3526	6	18	
Barometer 757 (756·8) mm.	0·3526	6	20	
Temp. of the room 14°.	0·3526(7)	7 minutes		
5. { −40 c.c., + 40 c.c. KCl. (sol. 0·076064 mol. norm.)	0·2223	7	0	*5·40
Bath −1·8°.	0·2222			
Barometer 757 mm.	0·2221	7	2	
Temp. of the room 14°. †	0·2221			
	0·2220	7	5	
	0·2220			
	0·2221	7	8	
‡	0·2221	8 minutes		
5′. Bath −1·8°.	0·2218	8	0	*5·23
Barometer 757 mm.	0·2217	8	2	
Temp. of the room 14·3°.	0·2219	8	4	
	0·2218	8	7	
†	0·2217	8	10	
‡	0·2217	10 minutes		

* Reading of small thermometer before the freezing of the solution.
† No formation of ice on thermometer or stirrer.
‡ Sufficient formation of ice. § Ice formed on the thermometer and stirrer.

heat and the latent heat of fusion of the dilute solution are the same as those of pure water. This mode of correcting is doubtless the safest and the most convenient; certainly it is to be preferred to the correction obtained by removing the ice and determining the density of the residual solution. In the experiments made by Loomis, who used a liquid bath and small quantities of solution, it is possible that the rapid cooling caused more ice to be formed than the theory indicates; but this cannot be the case in the above-mentioned experiments, where an air bath was used, and large quantities of solution were employed. As the total correction is small, the error introduced in making the correction as described can only be very minute.

For the corrections of reading for variations of atmospheric pressure, see p. 9.

For the corrections of the freezing point of water and of aqueous solutions in experiments in which the thermometer bulb was surrounded by a film of ice, see footnote, p. 6.

Before giving some of the results obtained, to serve as an illustration of the method, the mode of *calibrating* the more delicate thermometer may be described.

The operation was performed by reading the positions l and r of the two ends of a detached thread of mercury on the scale. A thread suitable for this purpose was obtained by heating the thermometer to some degrees above the temperature of the room, so that a sufficient quantity of mercury passed over into the lower part of the upper reservoir; on allowing the thermometer to cool, the mercury retreated into the bulb; a small quantity of mercury was then made to pass from the upper reservoir into the capillary in the same way as that commonly used in adjusting a Beckmann thermometer.

The small thermometer was an unusually fine instrument, tested in the Berlin Observatory, and found to be quite correct; it was used by Götze as a standard of comparison for his other thermometers.

In the following table
a = concentration of the solution taken in gram molecule per litre.
α = depression of the freezing point.
b = cooling of the liquid below the freezing point.
c = percentage weight of solvent (water), which crystallises out when the solution is super-cooled = b.
d = concentration actually subsisting after the separation of the quantity of solvent stated under c.
α_1 = corrected value of α.
β = molecular depression = $\frac{\alpha}{\alpha_1}$.
$\frac{i-1}{2} \times 100$ = percentage of substance dissociated.
E = number of experiments from which the data for water and solution are obtained.

Van't Hoff's constant for water is 1·89.

Depression of the Freezing Point in very Dilute Solutions of Potassium Chloride.

E.	a. Mol. norm.	a. Depress. obs.	b.	c.	d. = factor × $a10^5$.	a_1 10⁵.	$\beta = \frac{a}{a_1}$.	$i = \frac{\beta}{1·89}$.	$\frac{i-1}{2}$. 100.
1 n. 2	0·009711	0·0352	0·867	1·084	$\frac{100}{98·92} \times a =$	981·8	3·585	1·897	89·7
1′ n. 2′	0·009711	0·0349	0·912	1·14	$\frac{100}{98·86} \times a =$	982·2	3·553	1·88	88·0
1 n. 3	0·01934	0·0677	0·839	1·111	$\frac{100}{98·89} \times a =$	195·6	3·472	1·837	83·7
1′ n. 3′	0·01934	0·0676	0·822	1·027	$\frac{100}{98·97} \times a =$	195·4	3·459	1·83	83·0
1 n. 4	0·03845	0·13565	0·811	1·014	$\frac{100}{98·99} \times a =$	388·4	3·1925	1·848	84·8
1′ n. 4′	0·03845	0·13495	0·792	0·990	$\frac{100}{99·01} \times a =$	388·3	3·476	1·839	83·9
1 n. 5	0·076064	0·26555	0·481	0·6012	$\frac{100}{99·40} \times a =$	765·2	3·470	1·836	83·6
1′ n. 5′	0·076064	0·26585	0·651	0·8138	$\frac{100}{99·19} \times a =$	766·8	3·467	1·835	83·5

II.—*Corydaline.* Part IV.

By James J. Dobbie, M.A., D.Sc., and Alexander Lauder.

Specific Rotation of Corydaline.

The specific rotatory power of corydaline in alcoholic solution was determined, with the following results.

I.

d = sp. gr. of solution 20°/4° = 0·8160; p = percentage of corydaline in 100 grams solution = 0·9457; c = concentration = dp = 0·7716; l = 2 decimetres; α = rotation at 20° = +4·8°.

$$[\alpha]_D = \frac{\alpha \times 100}{lc} = \frac{4{\cdot}8 \times 100}{2 \times 0{\cdot}7716} = +311{\cdot}0.$$

II.

d 20°/4° = 0·8167; p = 1·0185; c = dp = 0·8318; l = 2 decimetres; α at 20° = +5·15°.

$$[\alpha]_D = \frac{\alpha \times 100}{lc} = \frac{5{\cdot}15 \times 100}{2 \times 0{\cdot}8318} = +309{\cdot}5.$$

Action of Chlorine on Corydaline.—A chlorinated derivative of corydaline was accidentally obtained in the following manner. In recovering the unoxidised corydaline from the manganese dioxide obtained in the process of oxidation, this oxide was exhausted with alcohol, the alcoholic solution evaporated to dryness, and the residue treated with hydrochloric acid. A little manganese dioxide had passed through the filter, and this gave rise to an evolution of chlorine, which attacked the corydaline and converted it into a monochloro-derivative. This is easily soluble in water, from which it crystallises, on slow evaporation, in large, golden yellow, prismatic crystals. Its hot aqueous solution, acidified with hydrochloric acid, deposits it in magnificent, golden spangles, on cooling. It melts at 188—191°, and decomposes a little above this temperature. It is sensitive to light, darkening after a short exposure. It was dried at 100°, and the chlorine determined.

I. 0·2912 gave 0·1052 AgCl. Cl = 8·93.
II. 0·2627 ,, 0·0936 AgCl. Cl = 8·80.
$C_{22}H_{28}ClNO_4$ requires Cl = 8·75 per cent.

Oxidation with Potassium Permanganate (continued).

In our first paper on the oxidation of corydaline with potassium permanganate (Trans., 1894, 65, 57), we stated that when the mother liquor, from which the corydalinic acid had been removed by crystallisation, was evaporated, it yielded a clear, yellow, resinous substance; this, when dissolved in water and precipitated with lead acetate or silver nitrate, yielded the corresponding salt or salts of an organic acid or acids. We have now examined this precipitate, and find that, in addition to a little corydalinic acid, it consists chiefly of hemipinic acid mixed with a small quantity of a nitrogenous acid and uncrystallisable matter.

The mother liquors, from which the corydalinic acid had been extracted as completely as possible, were neutralised with ammonia, and lead acetate added until precipitation was complete. The precipitate, after being thoroughly washed with water, was decomposed with hydrogen sulphide, and the solution filtered from the lead sulphide and concentrated by evaporation. A little corydalinic acid first separated, being much less soluble than the other oxidation products; the filtrate from this, when further concentrated, very slowly deposited a mass of crystals, which were separated with difficulty from the thick, syrupy liquid by means of the filter pump. These crystals, purified by repeated crystallisation from water, were found to be separable into two fractions, the less soluble portion, which crystallised in long, prismatic crystals, melting between 170° and 180°. It was further purified by reprecipitation with lead acetate, and subsequent decomposition of the lead salt with hydrogen sulphide. The crystals, which were free from nitrogen, were dried at 100° and analysed.

I. 0·2862 gave 0·5552 CO_2 and 0·1235 H_2O. C = 52·91; H = 4·79.
II. 0 2285 „ 0·4402 CO_2 „ 0 0932 H_2O. C = 52·54; H = 4·53.
$C_{10}H_{10}O_6$ requires C = 53·09; H = 4·42 per cent.

The silver salt was prepared by neutralising the aqueous solution of the acid with ammonia, and precipitating with silver nitrate. It was dried at 100° for analysis.

I. 0·2557 gave 0·1251 Ag. Ag = 48 93.
II. 0·2765 „ 0 1354 Ag. Ag = 48·96.
$C_{10}H_8O_6Ag_2$ requires Ag = 49 09 per cent.

On treating the acid with fuming hydrogen iodide, methylic iodide was formed. The methoxy-groups were determined by Zeisel's method in the usual manner.

I. 0·2439 gave 0·4591 AgI. OCH_3 = 26·80.

Theory for two methoxy-groups in $C_{10}H_{10}O_6$ requires 27·43 per cent. OCH_3.

These results prove that the substance is one of the varieties of hemipinic acid. We experienced the same difficulty as others in determining the melting point of this acid. Specimens prepared at different times, or obtained at different stages of the operations, when examined separately, appeared to melt at temperatures differing by as much as 10°, but the same specimens were found, when examined side by side, to decompose exactly at the same temperature. The melting point which we most frequently observed was 174—175°, the melting point given by Goldschmidt for metahemipinic acid from papaverine (*Ber.*, 1888, **21**, Ref. 786), but it is impossible to rely on this property as a means of identifying the acid. Goldschmidt states that the melting point of the hemipinic acid from narcotine varies between 156° and 158° in a closed capillary tube, and between 160° and 161° in an open capillary tube, the highest melting point observed on quickly heating being 182°; the melting point of metahemipinic acid from papaverine, on the other hand, varies between 172° and 173·5° in a closed, and between 174° and 175° in an open capillary tube, the highest melting point observed on rapidly heating being 194°. Perkin, again, found that the hemipinic acid he obtained from berberine melted sometimes between 159° and 160°, and sometimes between 177° and 178°. With the view of determining whether the acid which we had obtained was identical with the hemipinic acid from narcotine or with metahemipinic acid from papaverine, we subjected it to the various tests given by Goldschmidt (*loc. cit.*), and by Perkin (Trans., 1889, **55**, 63). Specimens of the acid prepared at different times and under different conditions were found to be free from water of crystallisation; isolated, well-developed crystals were frequently obtained, and invariably presented the form of monoclinic prisms. When treated with ferric chloride, an aqueous solution of the acid gave an orange-yellow coloration. The anhydride was prepared by heating 1 gram of the acid for about an hour at 200° and dissolving the residue in glacial acetic acid, from which the anhydride crystallises in delicate, colourless needles, melting sharply at 166—167°. The solution of the anhydride in acetic acid, especially when dilute, shows a beautiful, blue fluorescence. This substance was dried at 100° and analysed.

I. 0·1149 gave 0·2439 CO_2 and 0·0412 H_2O. C = 57·88; H = 3·98.
$C_{10}H_8O_5$ requires C = 57·69; H = 3·84 per cent.

As the melting points of the ethylimide of hemipinic and metahemipinic acids respectively differ by more than 130°, this derivative affords an excellent means of distinguishing between the two acids. Some of this substance was therefore prepared by the method given by C. Liebermann (*Ber.*, 1886, **19**, 2275). 1 gram of the pure acid was dissolved in an aqueous solution of ethylamine, evaporated to dryness, the residue heated over the naked flame, and then exhausted with boiling methylic alcohol; on cooling, the ethylimide separated in beautiful, long, needle-shaped crystals, melting at 90°. By recrystallising twice from boiling water, the melting point was raised to 92°. The melting point given by Liebermann for the ethylimide of hemipinic acid is 96°. There can be little doubt, therefore, that the hemipinic acid from corydaline is identical with that obtained from narcotine and berberine, and has the formula $C_6H_2(OCH_3)_2(COOH)_2$ [= 1 : 2 : 3 : 4]. It agrees with this acid in crystalline form, in its reaction with ferric chloride, and in the melting point of its anhydride. According to Goldschmidt, the hemipinic acid from narcotine contains $2H_2O$, but Perkin found (Trans., 1889, 55, 63) that the acid obtained from berberine, which is undoubtedly identical with that from narcotine, crystallised sometimes with and sometimes without water of crystallisation. We noticed that the acid sometimes separated quickly and completely from its aqueous solution, at other times only after long standing, a peculiarity also remarked by Perkin in the case of the hemipinic acid obtained from berberine.

After the removal of the hemipinic acid from the mother liquors of corydalinic acid, a small quantity of a nitrogenous acid was obtained; this is very soluble in water, melts sharply at 156°, and gives a white precipitate with silver nitrate. It crystallises from its concentrated aqueous solution in tufts of delicate, silky needles. We have not yet succeeded in obtaining this acid in sufficient quantity for analysis.

When the hemipinic and other acids had been removed as completely as possible by means of lead acetate, the filtrate from the lead precipitate was evaporated to a small bulk. After a lapse of several days, a crop of minute, colourless crystals was deposited; these separated from the thick, gummy mother liquor by means of the filter pump, were recrystallised several times from water or alcohol, in both of which they are freely soluble. The crystals, which sometimes attain a considerable size ($\frac{1}{8}$ of an inch), have the appearance, when properly developed, of oblique prisms. They contain no water of crystallisation, and melt sharply at 175°. Their aqueous solution is neutral to test paper. For analysis, it was dried at 100°.

I. 0·2394 gave 0·5549 CO_2 and 0·1393 H_2O. C = 63·21; H = 6·46.
II. 0·2480 „ 0·5753 CO_2 and 0·1509 H_2O. C = 63·27; H = 6·76.
III. 0·2844 „ 0·1361 Pt. N = 6·90.
IV. 0·2936 „ 0·1373 Pt. N = 6·74.

Mean of the above C = 63·24; H = 6·61; N = 6·82 per cent.; from which we deduce the formula $C_{11}H_{13}NO_3$; this requires C = 63·76; H = 6·28; N = 6·76 per cent. The methoxy-groups were determined by Zeisel's method in the usual way.

I. 0·2326 gave 0·5210 AgI = 29·57 per cent. OCH_3.
II. 0·2103 „ 0·4714 AgI = 29·59 „ „

Theory for two OCH_3 groups in $C_{11}H_{13}NO_3$ = 29·95 per cent. OCH_3. The formula of this substance is therefore probably $C_9NH_7(OCH_3)_2O$.

With the view of determining whether this compound contains an aldehydic or ketonic group, we tried to form a compound of it with phenylhydrazine. One gram of the substance was treated with a mixture of phenylhydrazine and sodium acetate, but no compound was obtained even after warming the mixture, and allowing it to stand for a considerable time. As, however, the amount of material at our disposal was only sufficient for one experiment, and we were unable to vary the conditions, we cannot attach much importance to this negative result. With rosaniline, decolorised with sulphurous acid, we obtained a distinct, though feeble, reaction. We shall therefore for the present refer to this substance under the name of *corydaldine.*

We were unfortunately unable to control the molecular weight of corydaldine by the formation of derivatives. As, however, it only contains one atom of nitrogen, and the analyses are quite satisfactory, there can be little doubt that the formula given is the correct one. The determination of the methoxy-groups affords further confirmation of its correctness.

When heated with lime, corydaldine gives the odour characteristic of the quinoline bases. An aqueous solution of corydaldine gradually reduces a solution of silver nitrate when the mixture is heated.

In addition to the oxidation products already mentioned, we obtained small quantities of at least two other substances, but not sufficient to enable us to give any account of them.

Action of Hydrogen Iodide on Corydalinic acid.—In our first paper on the oxidation of corydaline (Trans., 1894, **65**, 57), we described one product, corydalic acid, obtained by the action of hydrogen iodide on corydalinic acid, and mentioned the existence of other products which we had not then examined. We have now studied this action more fully, and find that three acids are produced when corydalinic acid is decomposed in this way—two non-nitrogenous and one nitrogenous, the last in very small quantity, the greater part of the nitrogen being eliminated as ammonia. The various products resulting from the decomposition were separated from one another by fractional crystallisation; corydalic acid being less soluble than the other acids separated out first. The mother liquors of the corydalic acid yielded a mass of fine needle-shaped crystals of a non-nitrogenous acid; this acid, which is the product of decomposition occurring in largest amount, decomposes sharply with effervescence at

199—200°, but without charring. Its aqueous solution is strongly acid, gives the pyrocatechol reaction with ferric chloride, and reduces an ammoniacal solution of silver nitrate. It is easily soluble in alcohol and in ether, but is practically insoluble in boiling benzene. The acid was dried at 100° for analysis.

I. 0·2768 gave 0 5553 CO_2 and 0·1086 H_2O. C = 54·71; H = 4·35.
II. 0·2619 „ 0·5270 CO_2 and 0·0996 H_2O. C = 54·88; H = 4·22.
$C_7H_6O_4$ requires C = 54·54, H = 3·89 per cent.

These results, taken in conjunction with the melting point of the acid, its insolubility in boiling benzene, and the reaction with ferric chloride, led us to suspect its identity with protocatechuic acid, which has the same formula. Protocatechuic acid crystallises with $1H_2O$. A specimen of the acid, dried over sulphuric acid until constant in weight, was heated at 100° until constant, with the following result.

I. 1·0961 lost 0 1098 H_2O at 100°. H_2O = 10·01.
$C_7H_6O_4H_2O$ requires H_2O = 10·46 per cent.

The lead salt, obtained by adding lead acetate to an aqueous solution of the acid, gave the following result on analysis.

I. 0·3088 gave 0·2920 $PbSO_4$. Pb = 64·58.

$Pb(C_7H_5O_4)_2,2PbO$, the salt obtained from protocatechuic acid under similar conditions, requires Pb = 64·75 per cent.

As a further means of identification, we subjected some of the acid to dry distillation; carbonic anhydride was evolved, and a solid residue obtained, which, after crystallisation from boiling benzene, gave all the reactions of pyrocatechol.

Further examination of the other non-nitrogenous acid, described in our last paper under the name of corydalic acid, has shown that the specimens on which our descriptions were based were not quite pure. Corydalic acid, when pure, crystallises in flat, prismatic crystals which decompose with effervescence at 178—180°, the residue melting completely to a dark brown liquid at about 250°; when heated with lime, it gave no odour of phenol. This acid is soluble in water, but less so than protocatechuic acid; it is also easily soluble in alcohol. Its aqueous solution is strongly acid, and gives the pyrocatechol reaction with ferric chloride. Its solutions immediately reduce an ammoniacal solution of silver nitrate in the cold, and a solution of copper acetate on heating. With silver nitrate in concentrated solutions, and with lead acetate in dilute solutions, it gives a copious white precipitate. Barium chloride gives no precipitate until the acid has been neutralised with ammonia, when a white precipitate is thrown down. Sodium hydroxide imparts a bright yellow colour to an aqueous solution of the acid, which becomes pale pink or almost colourless on heating, the yellow colour reappearing as the liquid cools. The analysis of the purified acid gave results differing slightly from those already published.

I. 0·1916 gave 0·3147 CO_2 and 0·0727 H_2O. C = 44·79; H = 4·21.
II. 0·2245 „ 0·3704 CO_2 and 0·0815 H_2O. C = 44·99; H = 4·03.

These analyses were made on different preparations of the acid. Mean of above results C = 44·89; H = 4·12 per cent. These numbers agree better with the formula $C_7H_8O_6$ than with the formula $C_9H_{10}O_8$ which we gave in our last paper. Theory for $C_7H_8O_6$, C = 44·68 per cent.; H = 4·25 per cent.

The lead salt, prepared by adding lead acetate to an aqueous solution of the acid, was analysed with the following result.

I. 0·2585 gave 0·2353 $PbSO_4$. Pb = 62·16 per cent.

This agrees fairly well with the analyses previously published, namely, 63·02 and 62·53 per cent.

The silver salt was prepared by adding silver nitrate to a concentrated aqueous solution of the acid. A white curdy precipitate, with a tendency to gelatinise, was obtained. It is somewhat solüble in water. Dried at 100°, it gave the following result.

I. 0·1690 gave 0·0611 Ag. Ag = 36·15 per cent.

If the formula given for the acid is correct, these results, as well as those previously published, agree best with the view that the acid is tribasic, or, at all events, contains three replaceable atoms of hydrogen. The percentage of silver found would then correspond with that required for the mono-silver salt, and the percentage of lead with that required for the normal lead salt.

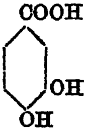
	Theory for $(C_7H_7O_6)Ag$.	Found.
Ag..........	36·60 per cent.	36·15 per cent.

	Theory for $(C_7H_5O_6)_2Pb_3$.	Found.
Pb..........	62·66 per cent.	62·16 per cent.

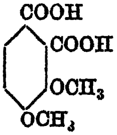
It is impossible, however, in the absence of further data, to determine the basicity of this acid satisfactorily. We have not succeeded in identifying corydalic acid with any of the known acids of the formula $C_7H_8O_6$.

The mother liquors from which the protocatechuic and corydalic acids had been removed, yielded a small quantity of a nitrogenous acid of high melting point, when concentrated. On evaporating the mother liquor from this acid to dryness and heating the residue with soda, ammonia was given off in abundance.

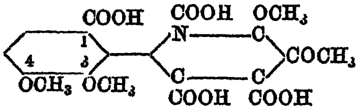
Although many points in the constitution of corydaline remain to be cleared up, the results which we have obtained bring us nearer to a solution of the problem. As we pointed out in our last paper, the constitution of corydalinic acid is most easily explained on the assumption that it is a derivative of phenylpyridine containing four carboxyl groups and four methoxy-groups. This view is now confirmed, and definite information has been obtained, both as to the distribution of the carboxyl and methoxy-groups, and as to their arrangement relatively to one another. The formation of protocatechuic acid from corydalinic acid shows that the non-nitrogenous part of the latter acid has one carboxyl and two methoxy-groups attached to it, and that these groups occupy the positions [COOH : OH : OH = 1 : 3 : 4]; whilst the occurrence of hemipinic acid amongst the oxidation products proves that the nitrogenous ring must be connected with the non-nitrogenous ring through the carbon atom occupying the position 2.



Protocatechuic acid.



Hemipinic acid.



Corydalinic acid.

It follows that the nitrogenous nucleus of corydalinic acid contains two methoxy-groups. This conclusion is confirmed by the analysis of corydaldine, $C_9NH_7(OCH_3)_2O$, which contains the nitrogenous nucleus of corydaline and also two methoxy-groups. Although we have not yet determined the constitution of corydaldine, there can be little doubt that it is an oxy-derivative of isoquinoline. Freund and Josephi (*Annalen, loc. cit.*), from the analogies of corydaline to hydrohydrastinine, infer the existence of a reduced isoquinoline group in corydaline. The oxidation of this group would account for two of the carboxyl groups of corydalinic acid, whilst if we accept the further suggestion of the same chemists that there is a methyl group attached to the nitrogen atom, the oxidation of this group would account for the fourth carboxyl group, and the constitutional formula of corydalinic acid would be that which is given above, the relative positions of the nitrogen atom and the methoxy-groups in the pyridine nucleus being still undetermined.

It seems probable that corydalic acid results from the splitting up of the nitrogenous portion of corydalinic acid; the view expressed in our last paper, that it is formed from the non-nitrogenous ring, being rendered untenable by the discovery of protocatechuic acid amongst the decomposition products of corydalinic acid. So far as we are aware, the action of hydrogen iodide on the pyridinecarboxylic acids has not yet been studied, except in one or two cases; but it is well known that on reduction with sodium amalgam the nitrogen is eliminated as ammonia, non-nitrogenous acids being formed. In the case of corydalinic acid, it is certain that, at least, part of the nitrogen is eliminated as ammonia, and it is probable that corydalic acid represents the residue of that portion of the substance.

Corydaline appears to be constituted similarly to papaverine, hydrastine, and narcotine, with this difference, that the benzene ring is united directly with the quinoline nucleus, instead of through an intervening carbon atom. We are still engaged in this investigation, and expect soon to be in a position to publish further information with regard to those substances referred to in this paper which have not yet been completely examined, and to give the results obtained by other methods of experimenting.

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III.—*The Alkaloïds of* Corydalis cava—*Corybulbine.*

By James J. Dobbie, M.A., D.Sc., and Alexander Lauder.

In a paper which appeared in the *Berichte* (**25**, 2411), Messrs. Freund and Josephi mentioned that they had obtained from the crude corydaline supplied to them by Schuchardt, of Görlitz, a small quantity of an alkaloïd melting at 205—207°, and soluble in caustic alkali. We supposed this alkaloïd to be identical with that which we subsequently described under the name corytuberine (Trans., 1893, **63**, 485), but we find from a more recent paper by the same authors (*Annalen*, **277**, 1), that the alkaloïd referred to by them was quite distinct from corytuberine, which was therefore isolated as well as described for the first time by us.

The quantity of material which Freund and Josephi had at their disposal was insufficient for more than a slight examination of the properties of the new alkaloïd, to which they gave the name of corybulbine, and they have, therefore, left the fuller investigation of it in our hands.

Corybulbine is obtained from Schuchardt's crude corydaline by the following method. After the corydaline has been thoroughly exhausted with boiling water to remove the corytuberine, the residue, which consists of corydaline mixed with a small quantity of corybulbine, is repeatedly exhausted with hot alcohol, which easily removes the corydaline. The crude corybulbine is then dissolved in a large quantity of boiling alcohol, from which it separates, on cooling, in the form of a fine crystalline deposit, leaving the remainder of the corydaline in solution. The corybulbine obtained in this way is collected, dried, and dissolved in hot dilute hydrochloric acid. The acid solution, on cooling, deposits the hydrochloride, which, after recrystallisation, is dissolved in boiling water with the aid of a little hydrochloric acid, and the corybulbine, precipitated from this solution by the addition of ammonia, is finally crystallised from alcohol. This method of preparation affords an excellent means of separating corybulbine from the last traces of corydaline, the hydrochloride of which is much more easily soluble in water than that of the new alkaloid.

Corybulbine may also be prepared from the crude material, after freeing it from corytuberine, by dissolving it in hydrochloric acid, and precipitating the corydaline with excess of a solution of sodium hydroxide; the filtrate from the corydaline, when saturated with carbon dioxide, deposits the corybulbine.

Corybulbine is soluble in boiling alcohol, from which it separates, on cooling, as a fine crystalline powder. It is practically insoluble in water, and nearly so in ether; it is sparingly soluble in boiling methylic alcohol, readily in carbon bisulphide, chloroform, and hot benzene. It is distinguished from corydaline and corytuberine, as well as from the bases described by Freund and Josephi (*Annalen*, **277**, 1) by its greater insolubility in alcohol. An alcoholic solution of the alkaloïd rapidly reduces a solution of silver nitrate when heated with it. Corybulbine begins to soften at 210°, but does not melt till heated to 238—240°. Freund and Josephi state that the alkaloïd softens at about 200°, and decomposes at 207—208°, but they sometimes found the melting point some degrees higher. A solution of the alkaloid in chloroform is dextrorotatory.

We have not succeeded as yet in obtaining crystals of corybulbine sufficiently large to allow of our describing their form. All the specimens we have examined have been pale-yellow, but we are unable to state positively whether or not the colour is a property of the substance, or is due to slight decomposition, as in the case of corydaline.

The following are the results of the analysis of the alkaloïd, purified by repeated recrystallisation from alcohol, and dried at 100°.

I. 0·2167 gave 0·1382 H_2O. H = 7·08.
II. 0·2683 „ 0·7023 CO_2 and 0·1732 H_2O. C = 71·38; H = 7·17.
III. 0·2214 „ 0·5788 CO_2 and 0·1516 H_2O. C = 71·29: H = 7·60.
IV. 0·3211 „ 0·0891 Pt. N = 4·00 per cent.
V. 0·2993 „ 0·0849 Pt. N = 4·09 „

Mean of the above analyses:—C = 71·33; H = 7·28; N = 4·04 per cent. These numbers lead to the formula $C_{21}H_{25}NO_4$, which requires C = 70·99, H = 7·04, N = 3·94 per cent.

Corybulbine forms easily crystallisable salts with hydrochloric acid and sulphuric acid.

Corybulbine Hydrochloride.—This salt is prepared by dissolving the alkaloid in hot hydrochloric acid, from which it separates, on cooling, in clusters of thick, prismatic crystals. It requires a large quantity of boiling water for solution, but this is greatly facilitated by the addition of a little hydrochloric acid. The salt contains no water of crystallisation. It was dried at 100°, and a complete analysis of it made, to serve as a check on the analysis of the alkaloïd.

I. 0·2432 gave 0·5756 CO_2 and 0·1536 H_2O. C = 64·55; H = 7·01.
II. 0·2880 „ 0·0736 Pt. N = 3·68 per cent.
III. 0·2891 „ 0·1071 AgCl. Cl = 9·15 „
IV. 0·2679 „ 0·1011 AgCl. Cl = 9·33 „
V. 0·2052 „ 0·0769 AgCl. Cl = 9·26 „
$C_{21}H_{25}NO_4,HCl$ requires C = 64·36; H = 6·64; N = 3·57; Cl = 9·07 per cent.

The addition of a solution of potassium iodide to a solution of the hydrochloride in water, produces a pale yellow precipitate of the hydriodide, which is insoluble in cold, but readily soluble in hot water.

Corybulbine Sulphate.—The acid sulphate is obtained by dissolving the alkaloïd in hot dilute sulphuric acid. When the solution is allowed to cool slowly, long, prismatic, colourless crystals separate; it contains no water of crystallisation. It is somewhat more easily soluble in hot water than the hydrochloride. It was dried at 100°, and gave the following results on analysis.

I. 0·3517 gave 0·1763 $BaSO_4$. S = 6·88.
II. 0·3494 „ 0·1775 $BaSO_4$. S = 6·98.
$C_{21}H_{25}NO_4,H_2SO_4$ requires S = 7·06 per cent.

Corybulbine Platinochloride.—The platinochloride is obtained by adding a solution of hydrogen platinochloride to a solution of corybulbine hydrochloride in water. It is a pale yellow substance slightly soluble in water. It was dried at 100°, and gave the following results on analysis.

I. 0·2578 gave 0·0441 Pt. Pt = 17·10.
II. 0·3257 ,, 0·0560 Pt. Pt = 17·19.
III. 0·4445 ,, 0·0771 Pt. Pt = 17·34.

Those analyses were made on different preparations of the salt, mean Pt = 17·21 per cent. $(C_{21}H_{25}NO_4)_2,H_2PtCl_6$ requires Pt = 17·41 per cent.

When a solution of gold chloride is added to a solution of corybulbine hydrochloride in water, a flocculent, orange-coloured precipitate is obtained, but as this salt is readily decomposed we did not attempt to analyse it.

Corybulbine Methiodide.—This compound is prepared by digesting the alkaloïd with a mixture of absolute alcohol and methylic iodide, for several hours, in a flask having a reflux condenser attached to it. On evaporating the solution, the methiodide crystallises out in clusters of large, yellow, prismatic crystals, which were purified by recrystallisation from alcohol. After being dried at 100°, the iodine was determined with the following results.

I. 0·2862 gave 0·1327 AgI. I = 25·05.
II. 0·2590 ,, 0·1214 AgI. I = 25·33.
$C_{21}H_{25}NO_4 \cdot CH_3I$ requires 25·55 per cent. I.

Action of Hydrogen Iodide on Corybulbine.—When corybulbine is treated with a concentrated solution of hydrogen iodide (sp. gr. 1·7), methylic iodide distils over, and a yellow, crystalline compound separates from the liquid remaining in the flask. The methoxy-groups were determined by Zeisel's method with the following result.

I. 0·2091 gave 0·4032 AgI; 25·46 per cent. OCH_3.

Three methoxy-groups in $C_{21}H_{25}NO_4$ require OCH_3 = 26·19 per cent.

Corybulbine is the fifth alkaloïd which has now been separated from the tubers of *Corydalis cava.*

Bulbocapnine, $C_{19}H_{19}NO_4$.
Corycavin, $C_{23}H_{23}NO_5$.
Corydaline, $C_{22}H_{29}NO_4$.
Corytuberine, $C_{19}H_{25}NO_4$.
Corybulbine, $C_{21}H_{25}NO_4$.

In addition to the alkaloïds here enumerated, an amorphous substance of low melting point (65—75°) is mentioned by Freund and Josephi as having been obtained by Merck from the roots of *Corydalis cava,* but as it is doubtful whether it is homogeneous, we have omitted it from our list.

In their first paper on the alkaloïds of *Corydalis cava,* Freund and Josephi gave the formula $C_{34}H_{36}N_2O_7$ for bulbocapnine (*Ber.*, 25, 2412), but they have since altered it to $C_{19}H_{19}NO_4$. Although several of the

Name.	Formula.	Number of methoxy-groups.	Melting point.	Action on polarised light.	Solubility in				References.
					Water.	Alcohol.	Chloroform.	Caustic alkalis.	
1. Corydaline	$C_{22}H_{29}NO_4$	$C_{18}H_{17}N(OCH_3)_4$	134·5°	Dextrorotatory	Insoluble	Easily soluble	Easily soluble	Insoluble	Dobbie & Lauder, Trans., 1892, 61, 244 and 605.
2. Corybulbine	$C_{21}H_{25}NO_4$	$C_{18}H_{16}NO(OCH_3)_3$	238—240°	Do.	Do.	Sparingly soluble in boiling alcohol	Do.	Soluble	Dobbie & Lauder, this vol., p. 25.
3. Corytuberine ...	$C_{19}H_{25}NO_4$	$C_{17}H_{19}NO_2(OCH_3)_2$	200°?	Do.	Soluble in hot water	Soluble	Insoluble	Do.	Dobbie & Lauder, Trans., 1893, 63, 485.
4. Bulbocapnine ...	$C_{19}H_{19}NO_4$	$C_{18}H_{16}NO_3(OCH_3)$	199°	Do.	Insoluble	Do.	Easily soluble	Do.	Freund and Josephi, *Ber.*, 25, 2412; *Ann.*, 277, 1.
5. Corycavine ...	$C_{23}H_{23}NO_5$	—	214—215°	—?	Do.	Soluble in hot, but only sparingly in cold alcohol	—?	Insoluble	

alkaloïds mentioned above approach each other very closely in composition, they are easily distinguished by their reactions and by their behaviour when treated with hydrogen iodide. Thus, corytuberine alone is soluble in warm water: corybulbin, bulbocapnine, and corytuberine are all soluble in sodium hydroxide, whilst corydaline and corycavine are insoluble in both these solvents. The two last mentioned alkaloïds are distinguished from one another by the much greater solubility of the former in alcohol. Although there is a larger number of oxygen atoms in corycavine than in any other of these alkaloïds, it does not contain any methoxy-groups. Of the remaining alkaloïds, all of which contain four oxygen atoms, bulbocapnine has one, corytuberine two, corybulbine three, and corydaline four methoxy-groups. In a note to their paper in the *Annalen*, Freund and Josephi suggest that corytuberine may be identical with the corydalinnobiline obtained by Birsmann from *Corydalis nobilis* (*Inaug. Disser.*, Dorpat, 1892). A careful comparison of our results with those of Birsmann does not bear out this suggestion, the analysis, as well as the properties of the substance described by him, differing considerably from those of corytuberine; as, however, the quantity of material which Birsmann had at his disposal was insufficient for a thorough examination of his alkaloid, it is impossible to institute a perfectly satisfactory comparison between the two substances. If Birsmann really had corytuberine in hand, he could hardly have overlooked the powerful fluorescence of its aqueous solution

We subjoin a synopsis of some of the properties of those alkaloïds of *Corydalis cava* which have been most carefully examined.

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IV.—*The Yellow Colouring Matter of* Sophora japonica.

By Edward Schunck, Ph.D., F.R.S.

The undeveloped flower-buds of *Sophora japonica*, a leguminous plant growing in the north of China, contain a yellow colouring matter, which has been examined several times without any definite conclusion as to its nature having been arrived at. Stein (*J. pr. Chem.*, **58**, 399; **85**, 351; **88**, 280), as well as Spiess and Sostmann (*Arch. Pharm.*, **122**, 75), considered it to be identical with Rutin, the colouring matter contained in garden rue, buckwheat, and other plants. The subject was subsequently investigated by Foerster (*Ber.*, **15**, 214), whose experiments seemed to show that the colouring matter of the *Sophora* buds was a peculiar substance, to which he accordngly gave the name of *Sophorin*. I think, however, that I shall be able to prove that the older view is the correct one, and that Sophorin is indeed indentical with Rutin.

The greater part of the material employed in my experiments, I owe to the kindness of Mr. James Buchanan, of Shanghai. Mr. hiselton Dyer, Director of the Royal Gardens, Kew, supplied me th another portion, this having been obtained from plants grown in the open air at Kew. To those gentlemen I return my best thanks.

The yellow colouring matter of the *Sophora* flower-buds was obtained by simple extraction with boiling water, from which it crystallises in fine needles on cooling. It was purified by recrystallisation from boiling water, and had then the appearance and showed the reactions of Rutin as obtained from rue and other plants. Its pale, greenish-yellow colour, so different from the bright, lemon-yellow of quercitrin, is quite characteristic.

It dissolves in 190 parts of boiling water, it is easily soluble in alcohol, but insoluble in ether, chloroform, benzene, and carbon bisulphide. It dissolves in alkalis, giving bright, yellow solutions. The barium, calcium, lead, and tin compounds are yellow lakes. Analysis of the substance dried at 140° gave the following results.

0 1844 gave 0·3561 CO_2, 0·0830 H_2O. C = 52·67; H = 5·00.

These numbers agree with those previously obtained in the analysis of rutin from buckwheat leaves, which were as follows.

C	52·40 per cent.	52·55 per cent.
H	5·28 „	5·49 „

$C_{27}H_{32}O_{16}$ requires C = 52·97; H = 5·22 per cent.

When a watery solution of the substance to which sulphuric acid has been added is boiled for some time, it is decomposed; pale yellow, crystalline needles are deposited, and the liquid becomes almost colourless. The product insoluble in water, which Foerster calls "sophoretin," has the properties and composition of quercetin. After being purified by recrystallisation and dried at 130°, its analysis yielded the following results.

0·4466 gave 0·9720 CO_2 and 0·1440 H_2O. C = 59·33; H = 3·59.

The formula $C_{15}H_{10}O_7$, which, according to Herzig (*Monatsh.*, **12**, 172 and 177; **14**, 39 and 53), is the correct formula for quercetin, requires C = 59·60; H = 3 31 per cent.

The acetyl derivative of the substance, prepared in the usual manner, was found to have a melting point of 195°, and gave on analysis,

		Acetylsophoretin (Foerster).
C	58·32 per cent.	58·53 per cent.
H	4·16 „	4·38 „

Assuming it to be a pentacetyl compound, it should contain C = 58·47; H = 4·09 per cent. On treatment with dilute sulphuric acid, this acetyl derivative yielded 58·76 per cent. of regenerated substance; calculation requires 58·80 per cent.

The substance gave a crystallised bromine derivative, which was found to contain 34·54 per cent. bromine, calculation requiring Br = 34·77 per cent. for the formula $C_{15}H_8Br_2O_7$.

The filtrate from the product of decomposition of the colouring matter with sulphuric acid, after removal of the acid and evaporating, yields a crystallised sugar having all the properties of rhamnose. The decomposition of the substance would, therefore, be represented by the following equation.

$$C_{27}H_{32}O_{16} + 3H_2O = C_{15}H_{10}O_7 + 2C_6H_{14}O_6.$$

That is, it yields 1 mol. of quercetin and 2 mols. of rhamnose, quercitrin yielding 1 mol. of quercetin and 1 mol. of rhamnose. The quantity of quercetin which it should give in accordance with the above equation is 49·34 per cent. Two separate determinations gave 49·07 and 49·56 per cent. respectively.

Hence it appears that sophorin and rutin are, in fact, identical, and the former name may, therefore, be removed from the list of organic colouring matters.

V.—*Interaction of* 1 : 2-*Diketones with Primary Amines of the General Formula,* $R'\cdot CH_2\cdot NH_2$.

By Francis R. Japp, F.R.S., and W. B. Davidson, M.A., B.Sc.

Introduction.

The action of paraffinoid amines on 1 : 2-diketones appears to have been very little studied. Zincke and Hof (*Ber.*, **12**, 1641), by heating phenanthraquinone with methylamine, obtained a base to which they assigned the formula $C_{14}H_8(N\cdot CH_3)_2$, together with another compound, the composition of which they could not determine with certainty. Henius (*Ammoniakderivate des Benzils*, Marburg, 1881), desirous of studying the analogous interaction with benzil, heated that substance with methylamine, but obtained only a resinous product.

We shall show in the present paper that Zincke and Hof's base has not the foregoing composition. We have not repeated Henius's experiment with benzil and methylamine; but we find that benzil and ethylamine, under suitable conditions, readily yield a crystallised product.

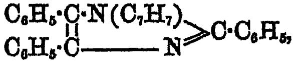
We first, however, investigated the interaction of benzil and benzylamine. When these two substances were heated together at 100°, a product was obtained from which we could isolate tetraphenylazine, $C_{28}H_{20}N_2$ (m. p. 246°), and a feebly basic compound melting at 164° and having the formula $C_{28}H_{22}N_2$: the latter substance being formed according to the equation,

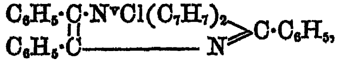
$$C_{14}H_{10}O_2 + 2C_6H_5\cdot CH_2\cdot NH_2 = C_{28}H_{22}N_2 + 2H_2O + H_2.$$

When zinc chloride was added to the mixture of benzil and benzylamine before heating, the same two compounds were obtained, but, in addition, a chloride of the formula $C_{35}H_{29}N_2Cl$ (m. p. 253°), formed according to the equation,

$$2C_{11}H_{10}O_2 + 6C_6H_5\cdot CH_2\cdot NH_2 + ZnCl_2 = 2C_{35}H_{29}N_2Cl + \\ 2NH_3 + Zn(OH)_2 + 2H_2O + 2H_2.$$

As the difference between the formula of the chloride, $C_{35}H_{29}N_2Cl$, and that of the base, $C_{28}H_{22}N_2$, is C_7H_7Cl, which might represent a molecule of benzylic chloride, we heated the base with benzylic chloride, and found that these two substances readily united to form the chloride $C_{35}H_{29}N_2Cl$. The base was therefore a tertiary amine, and the chloride was a quaternary chloride.

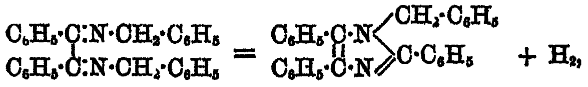
Suspecting that these two compounds were benzyl-derivatives of lophine, we next heated lophine with benzylic chloride. Both compounds were formed in this interaction. The base $C_{28}H_{22}N_2$ is therefore *benzyllophine*,  $\begin{array}{l} C_6H_5\cdot C\cdot N(C_7H_7) \\ \quad\;\, \| \\ C_6H_5\cdot C \text{———} N \end{array} \!\!> C\cdot C_6H_5$, and the chloride, $C_{35}H_{29}N_2Cl$, is *dibenzyllophonium chloride*,



$$\begin{array}{l} C_6H_5\cdot C\cdot N^{v}Cl(C_7H_7)_2 \\ \quad\;\, \| \\ C_6H_5\cdot C \text{————} N \end{array} \!\!> C\cdot C_6H_5,$$

the latter corresponding with Kühn's diethyllophonium iodide.*

When a mixture of benzil and benzylamine is dissolved in ether, and allowed to stand at the ordinary temperature, drops of water speedily separate, and, on allowing the ether to evaporate spontaneously, a gummy, uncrystallisable mass remains, which is probably the first stage in the condensation of benzil with benzylamine since, on heating at 100°, it yields benzyllophine. The change,



$$\begin{array}{l} C_6H_5\cdot C\colon N\cdot CH_2\cdot C_6H_5 \\ \quad\;\, | \\ C_6H_5\cdot C\colon N\cdot CH_2\cdot C_6H_5 \end{array} = \begin{array}{l} C_6H_5\cdot C\cdot N \\ \quad\;\, \| \\ C_6H_5\cdot C\cdot N \end{array} \!\!\begin{array}{l} \diagup CH_2\cdot C_6H_5 \\ \diagdown \\ \!\!> C\cdot C_6H_5 \end{array} + H_2,$$

is not without analogy. Thus, as Wallach has shown, the imidochloride obtained by the action of phosphorus pentachloride on diethyloxamide parts with hydrochloric acid yielding a base, chloroxalethyline, which, as was pointed out by one of us (*Ber.*, **15**, 2420), has the constitution of a chlorinated glyoxaline (imidazole) derivative,

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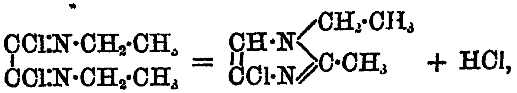
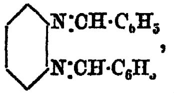
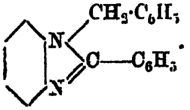
* Called by Kuhn "diethyllophinium iodide;" but we adopt Victor Meyer's suggestion (*Ber.*, 27, 505) that the names of all quaternary ammonium compounds and their analogues should end in "onium."

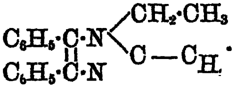


the position of the chlorine atom in the imidazole being uncertain.*

Again, in the case of the condensation products of orthodiamines with aldehydes, discovered by Ladenburg, the constitution of which was first explained by Hinsberg (*Ber.*, **19**, 2025), an analogous transformation occurs. Thus orthodiamidobenzene and benzaldehyde yield, instead of , the tertiary imidazole

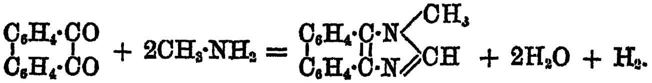


In order to ascertain whether the action of purely paraffinoid amines with benzil resembled that of benzylamine, we heated benzil with ethylamine and obtained N-ethyldiphenyl-μ-methyl-imidazole,



The quaternary chloride was also formed, but we did not succeed in isolating it in a state of purity. The constitution of the tertiary imidazole was proved by synthesising the compound from Japp and Wynne's diphenyl-μ-methyl-imidazole and ethylic iodide. It was also proved to be a tertiary amine by combining it directly with ethylic iodide.

As the results obtained by Zincke and Hof (*loc. cit.*) in studying the action of methylamine on phenanthraquinone differed from those which we had arrived at with benzil, we repeated their work. We had no difficulty in preparing the base described by them, but found that it gave, on analysis, figures pointing to the formula $C_{16}H_{12}N_2$, instead of $C_{16}H_{14}N_2$, as adopted by them. (No analyses are given by Zincke and Hof in the paper referred to.) The interaction with phenanthraquinone is, therefore, analogous to that with benzil, and the compound is, in all probability, N-*methyl-diphenylene-imidazole*,



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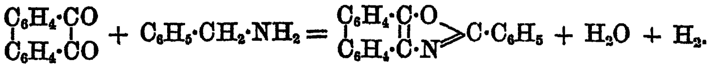
* In the original of the passage quoted, chloroxalmethyline is employed as an illustration, but the argument is of course identical.

An attempt to synthesise diphenylene-imidazole by the interaction of phenanthraquinone, formaldehyde, and ammonia, in order to prepare from it the foregoing compound, led to no result.

Phenanthraquinone and benzylamine give a different interaction, forming diphenylene-μ-phenyl-oxazole according to the equation



$$\begin{matrix}C_6H_4\cdot CO\\ |\quad\ \ |\\ C_6H_4\cdot CO\end{matrix} + C_6H_5\cdot CH_2\cdot NH_2 = \begin{matrix}C_6H_4\cdot C\cdot O\\ |\qquad \|\\ C_6H_4\cdot C\cdot N\end{matrix}\!\!>\!C\cdot C_6H_5 + H_2O + H_2.$$

At the same time, a sparingly soluble compound crystallising in bronze-coloured, microscopic, rectangular prisms is obtained, the exact composition of which we were unable to ascertain.

Diphenylene-μ-phenyl-oxazole was originally prepared by Japp and Wilcock (Trans., 1880, **37**, 668) by the interaction of phenanthraquinone, benzaldehyde, and ammonia, and named by them *benzenylamidophenanthrole*.

EXPERIMENTAL PART.

1. *Benzil and Benzylamine.*

The interaction of these two compounds was studied both with and without the addition of zinc chloride. We shall describe only the former method, as it gave the better result and furnished, moreover, a compound which was not otherwise obtained.

40 grams of benzil, mixed with 16 grams of powdered zinc chloride, were introduced into a flask, and 40 grams of benzylamine were added. The mixture became dark red, and considerable heat was evolved, due to the combination of the benzylamine with the zinc chloride. The flask was then heated at 100° for 40 hours, immersing it up to the neck in the water bath, as otherwise an equable heating of the pasty contents could not be effected. There was considerable frothing, ammonia being evolved during the process, and the colour of the mixture gradually changed from red to yellow. The product was then digested with boiling alcohol which dissolved everything except a white pulverulent substance; this proved to be a mixture of zinc hydroxide with a little tetraphenylazine. Acetic acid was then added in quantity sufficient nearly to clear the liquid; the still undissolved particles could then be seen to consist of slender needles; they were separated by filtration and identified as tetraphenylazine (ditolaneazotide), $C_{28}H_{20}N_2$, by their crystalline form, their melting point (247·5°), and the bright red coloration which they gave with concentrated sulphuric acid. The quantity obtained was 1·5 grams.

The formation of this compound may be readily accounted for. The other actions, occurring simultaneously (see Introduction), involve the elimination of hydrogen and ammonia; the former reduces a portion of the benzil to benzoïn, the latter converts the benzoïn into tetraphenylazine (compare Japp and Wilson, Trans., 1886, **49**, 829).

The alcoholic filtrate from the tetraphenylazine was concentrated by boiling, and then mixed with about four times its volume of ether. On standing, the liquid deposited lustrous crystals, of octahedral habit, whilst a substance, crystallising in square plates (see later), remained in the mother liquor. (If, as occasionally happened, some of these plates separated along with the octahedra, they could readily be removed by boiling the mixture of crystals with benzene, in which they dissolve readily, whilst the octahedra are quite insoluble.) The octahedra effloresced rapidly when exposed to air, and smelt strongly of ether; they contained ether of crystallisation. Freed from the ether, they melted at 248°. They contained both zinc and chlorine. The analyses, given later, showed that the compound was a double chloride of zinc and an organic base. The yield in the experiment here described was 17 grams.

A quantity of the octahedral crystals was dissolved in boiling alcohol, and the zinc was precipitated by the addition of aqueous sodium carbonate. The excess of sodium carbonate and the sodium chloride formed were thus mostly precipitated along with the zinc. The filtered and concentrated liquid deposited colourless, prismatic crystals, melting, when rapidly heated, at 253°. They were insoluble in water and in benzene, readily soluble in boiling alcohol. When treated with concentrated sulphuric acid, they evolved hydrochloric acid. A solution in alcohol gave, with silver nitrate, a precipitate of silver chloride. The chlorine is not removed by ammonia, although, as we shall show later, heating the compound with alcoholic caustic potash displaces the chlorine by hydroxyl. The substance, which is the chloride of a quaternary base, was purified by recrystallisation from alcohol and dried over sulphuric acid, as it decomposes slowly at a temperature slightly above 100°. It does not contain solvent of crystallisation. Analysis gave figures agreeing with the formula $C_{35}H_{29}N_2Cl$.

0·1590 gave 0·4770 CO_2 and 0·0823 H_2O. C = 81·82; H = 5·75.
0·1340 „ 0·4010 CO_2 „ 0·0700 H_2O. C = 81·61; H = 5·80.
0·2672 „ 12·4 c.c. moist nitrogen at 10° and 746·5 mm. N = 5·46.
0·8714 „ 0·2521 AgCl. Cl = 7·18.
$C_{35}H_{29}N_2Cl$ requires C = 81·95; H = 5·66; N = 5·46; Cl = 6·93 p. c.

Two other methods were employed in isolating the quaternary chloride from the zinc double compound. In one of these the latter compound was dissolved in hot alcohol and the zinc precipitated with ammonium sulphide; the filtered solution, after concentration, deposited the quaternary chloride. In the other, sodium acetate was added to the hot alcoholic solution, which was then diluted with water; the quaternary chloride slowly separated in a crystalline form, the zinc remaining in solution as acetate. Precipitation with sodium carbonate was found, however, to give the best results.

An alcoholic solution of the quaternary chloride gave, on addition of platinic chloride, also dissolved in alcohol, an orange-coloured, crystalline precipitate of the platinum salt. Under the microscope, the crystals were seen to consist of prisms terminated by pyramids. Sometimes these prisms were single, sometimes two were grouped into a right-angled cross, sometimes a third prism intersected the cross at right angles to its plane, forming a figure like the axes in the cubical system. We describe these forms thus particularly, inasmuch as we afterwards employed this salt in identifying the quaternary chloride. As the salt decomposes slowly at 80°, the air-dried substance was used for analysis.

1·2620 gave 0·1795 Pt. Pt = 14·22.
$(C_{30}H_{29}N_2Cl)_2PtCl_4$ requires Pt = 14·29 per cent.

By bringing together the chloride, $C_{35}H_{29}N_2Cl$, with zinc chloride in alcoholic solution, the zinc double compound could be regenerated. From alcohol, the double compound was deposited in well-formed crystals, without solvent of crystallisation. Although decomposed, as already mentioned, by sodium acetate, it can be recrystallised from glacial acetic acid without change.

A full analysis of the zinc double compound, as obtained in the original interaction, was made before its true nature had been ascertained, and before the organic chloride had been isolated from it. The substance was dried at 100°, so as to expel the ether of crystallisation. Of the various determinations, the carbon alone is not concordant, possibly owing to a difficulty in burning the substance; but the analysis was not repeated, as the quaternary chloride itself had meanwhile been obtained and analysed.

0·2494 gave 0·6544 CO_2 and 0·1150 H_2O. C = 71·56; H = 5·12.
0·3005 „ 13·2 c.c. moist nitrogen at 10° and 728·5 mm. N = 5·04.
6·2180 „ 0·4480 ZnO. Zn = 5·78.
1·1223 „ 0·5501 AgCl. Cl = 12·22.
$(C_{35}H_{29}N_2Cl)_2ZnCl_2$ requires C = 72·36; H = 4·99; N = 4·82; Zn = 5·60; Cl = 12·23 per cent.

The determination of the ether of crystallisation in the crystallised compound was a matter of some difficulty, owing to the rapidity with which the substance effloresced, and also owing to the fact that, occasionally, clear crystals, without solvent of crystallisation, were found among those which had been used for the determination, the latter form being, as already stated, that in which the double compound is deposited from alcohol without the addition of ether. The best result—only approximate, however—was obtained by taking for the determination a considerable weight (over 16 grams) of the substance deposited from alcohol on the addition of ether, avoiding the presence of small crystals, which were removed by sifting through coarse wire gauze, after the whole had been quickly dried on filter paper. The salt lost, on heating at 100°, 14·59 per cent., whilst the formula $(C_{35}H_{29}N_2Cl)_2ZnCl_2,3(C_2H_5)_2O$ requires 16·05 per cent. As the crystals had been deposited from a mixture of alcohol and ether, it was necessary to prove that the solvent of crystallisation consisted of ether only. For this purpose, some of the crystals, air-dried for a short time, were introduced into a distilling flask and the solvent of crystallisation distilled off on the water bath. The boiling point of the distillate was determined by Chapman Jones's method, from the vapour tension, and found to be 35°.

The ethereal-alcoholic mother liquor, containing those products of the original interaction which remained after the removal of the zinc double salt, was freed from its ether by distillation. The resulting alcoholic solution deposited, on long standing, yellow, square plates of a new compound, mixed, however, with needles of tetraphenylazine; the latter were removed by levigation. By recrystallising the square plates from benzene, in which they were readily soluble, and afterwards from alcohol, they were obtained colourless, and melted constantly at 165°. The substance is dimorphous; from concentrated solutions, it separates in slender needles; from dilute solutions, in square plates, as above; the presence of impurity appears to favour crystallisation in the latter form. Either form can be readily converted, by recrystallisation, into the other. The yield was about 20 grams. Analysis of the square plates dried at 100° gave figures agreeing with the formula $C_{28}H_{22}N_2$.

0·1358 gave 0·4325 CO_2 and 0·0709 H_2O. C = 86·86; H = 5·80.
0·1362 „ 0·4338 CO_2 „ 0·0722 H_2O. C = 86·86; H = 5·89.
0·1912 „ 11·90 c.c. moist nitrogen at 11° and 739 mm. N = 7·21.
0·1920 „ 12·13 „ „ „ 11·5° and 732·5 mm. N = 7·21.
$C_{28}H_{22}N_2$ requires C = 87·05; H = 5·70; N = 7·25 per cent.

The compound is insoluble in aqueous acids, but it nevertheless acts as a weak monacid base, forming a platinichloride. The latter is slowly deposited in large, lustrous, orange-coloured, oblique prisms, containing 3 mols. of alcohol of crystallisation, when concentrated solutions of the base and of platinic chloride (H_2PtCl_6) in absolute alcohol are mixed and allowed to stand. The crystals effloresced when exposed to the air. For analysis, they were air-dried for a short time. The figures for alcohol of crystallisation were not very concordant.

1·0882 (containing alcohol) lost, at 95°, 0·1250. $C_2H_5\cdot OH = 11\cdot49$.
$(C_{28}H_{22}N_2)_2H_2PtCl_6,3C_2H_5\cdot OH$ requires $C_2H_5\cdot OH = 10\cdot46$ per cent.
0 9632 (freed from alcohol) gave 0·1592 Pt. Pt = 16·53.
$(C_{28}H_{22}N_2)_2H_2PtCl_6$ requires Pt = 16·50 per cent.

The composition of this salt confirms the molecular formula, $C_{28}H_{22}N_2$, for the base.

Conversion of the Base, $C_{28}H_{22}N_2$, *into the Quaternary Chloride,* $C_{35}H_{29}N_2Cl$.—4 grams of the base were boiled for an hour with 8 grams of benzylic chloride in a flask fitted with a reflux condensing tube. During the process, a solid substance separated in acicular crystals. The product was digested with ether; the insoluble portion was separated by filtration, washed with ether, and dissolved in boiling alcohol. The alcoholic solution deposited crystals identical in form with those of the quaternary chloride, $C_{35}H_{29}N_2Cl$, mixed, however, with some of the unaltered compound, $C_{28}H_{22}N_2$; the latter substance was removed by boiling the mixture of crystals with benzene. The portion insoluble in benzene was purified by recrystallisation from alcohol until it showed the constant melting point of 253°. It was indistinguishable in appearance from the quaternary chloride obtained from benzil, benzylamine, and zinc chloride. In alcoholic solution, it gave a precipitate of silver chloride on the addition of alcoholic silver nitrate. A nitrogen determination confirmed the identity of the two substances.

0·3190 gave 14·7 c.c. moist nitrogen at 10° and 755 mm. N = 5·48.
$C_{35}H_{29}N_2Cl$ requires N = 5·46 per cent.

In addition, the platinum salt was prepared. It exhibited, under the microscope, the characteristic forms already described.

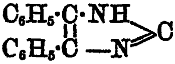
Synthesis of the Compounds $C_{28}H_{22}N_2$ *and* $C_{35}H_{29}N_2Cl$ *from Lophine.*—10 grams of lophine were boiled for an hour with 20 grams of benzylic chloride. Hydrochloric acid was evolved during the process. The product, which consisted of a crystalline mass saturated with excess of benzylic chloride, was washed several times with ether, uniting the ethereal washings. The crystalline portion was then recrystallised from alcohol until it melted constantly at 253°. It had all the properties of the quaternary chloride, $C_{35}H_{29}N_2Cl$, gave a precipitate with silver nitrate, and yielded the characteristic platinum salt. Nitrogen was determined with the following result.

0·2724 gave 12·8 c.c. moist nitrogen at 8° and 739·5 mm. N = 5·51.
$C_{35}H_{29}N_2Cl$ requires N = 5·46 per cent.

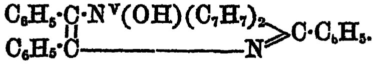
The ethereal washings were then heated to expel the ether, after which the excess of benzylic chloride was distilled off at 100° under reduced pressure. The residue, which was brown and crystalline, was dissolved in boiling alcohol. The solution deposited the two forms of the compound $C_{28}H_{22}N_2$, square plates and needles. The melting point was found to be 164·5° instead of 165°. A nitrogen determination, made with the square plates, gave figures agreeing with the expected formula.

0·2395 gave 15·3 c.c. moist nitrogen at 6° and 739·5 mm. N = 7·57.
$C_{25}H_{22}N_2$ requires N = 7·25 per cent.

The quantity of this compound obtained was very small, as, when formed, it is mostly converted into the quaternary chloride.

The two compounds are, therefore, benzyl derivatives of lophine (triphenylimidazole),  $\begin{matrix} C_6H_5{\cdot}C{\cdot}NH \\ \| \\ C_6H_5{\cdot}C\ -N \end{matrix}\!\!>\!C{\cdot}C_6H_5$, the base, $C_{28}H_{22}N_2$, being *benzyllophine*, and the chloride, $C_{35}H_{29}N_2Cl$, *dibenzyllophonium chloride*, as formulated in the Introduction to this paper.

Dibenzyllophonium Hydroxide.—8 grams of dibenzyllophonium chloride were dissolved in hot alcohol, 24 grams of powdered caustic potash were added, and the whole was digested on the water bath for 40 hours.* During the process potassium chloride separated. The alcohol was then driven off, and the residue treated with water, which dissolved everything except a brown substance. This was separated, first digested with a little alcohol, which removed most of the brown colour, and then dissolved in boiling alcohol. It separated in yellow square plates, which were purified by recrystallisation from boiling alcohol until they melted constantly at 170°. The substance is but sparingly soluble in alcohol, even at the boiling point of the solvent; readily, however, in boiling benzene, separating from it, on cooling, in forms identical with those obtained from alcohol, but always contaminated with pale brown needles of another substance (see later), so that benzene cannot be employed in its purification. The yellow colour is not removed by recrystallisation, or by treatment with animal charcoal. Analysis showed that the substance had the composition of *dibenzyllophonium hydroxide*,



$$\begin{matrix} C_6H_5{\cdot}C{\cdot}N^{V}(OH)(C_7H_7)_2 \\ \| \\ C_6H_5{\cdot}C\text{————————}N \end{matrix}\!\!>\!C{\cdot}C_6H_5.$$

0·1513 gave 0·4715 CO_2 and 0·0852 H_2O. C = 84·99; H = 6·26.
0·2517 ,, 11·9 c.c. moist nitrogen at 6° and 768·5 mm. N = 5·82.
$C_{35}H_{30}N_2O$ requires C = 85·02; H = 6·07; N = 5·67 per cent.

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* This long heating was possibly unnecessary, and, owing to the susceptibility of dibenzyllophonium hydroxide to aerial oxidation (see later), may even have diminished the yield.

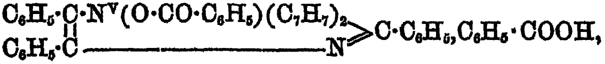
On dissolving the substance in alcoholic hydrochloric acid, the yellow colour disappeared, and the solution deposited colourless crystals which, by their form, melting point, and the characteristic platinum salt which they yielded, were identified as *dibenzyllophonium chloride*.

Benzoates of Dibenzyllophonium.—We have already mentioned that when dibenzyllophonium hydroxide is recrystallised from benzene, the solution deposits, along with the yellow, square plates of the hydroxide, pale brown needles of a different compound. Imagining that this was an impurity, we separated mechanically the crystals of the hydroxide, and redissolved them in benzene; but again the solution deposited a mixture of the two kinds; indeed, we found that, by repeatedly recrystallising the hydroxide from benzene, it could be completely transformed into the needles. The solubility of the latter was exactly the reverse of that of the hydroxide; they were sparingly soluble in benzene and readily in alcohol; for this reason, when alcohol was used in recrystallising the hydroxide, their presence was not perceived.

By recrystallising the needle-shaped compound from benzene, we obtained it almost colourless. It melted at 175·5°. Analysis gave figures agreeing with the formula $C_{49}H_{40}N_2O_4$.[*]

0·1708 gave 0·5111 CO_2 and 0·0880 H_2O. C = 81·61; H = 5·72.
0·1286 „ 0·3855 CO_2 and 0·0647 H_2O. C = 81·75; H = 5·59.
0·2547 „ 8·5 c.c. moist nitrogen at 7·5° and 759·5 mm. N = 4·04.
$C_{49}H_{40}N_2O_4$ requires C = 81·67; H = 5·56; N = 3·89 per cent.

This would be the composition of a *dibenzyllophonium dibenzoate* of the formula



$$\begin{array}{l} C_6H_5\cdot C\cdot N^{V}(O\cdot CO\cdot C_6H_5)(C_7H_7)_2 \\ \quad \| \\ C_6H_5\cdot C \text{———————————} N \end{array} \!\!> C\cdot C_6H_5, C_6H_5\cdot COOH,$$

formed from the hydroxide and benzoic acid according to the equation

$$C_{35}H_{29}N_2\cdot OH + 2C_6H_5\cdot COOH = C_{49}H_{40}N_2O_4 + H_2O.$$

In order to test the correctness of this supposition, a small quantity of dibenzyllophonium hydroxide was dissolved in benzene, after which twice its molecular proportion of benzoic acid was added. The yellow colour of the hydroxide disappeared instantly, and the liquid deposited colourless, needle-shaped crystals of the dibenzoate melting at 175°. They were purer than those obtained by the previous method. A nitrogen determination gave 4·00 per cent. ($C_{49}H_{40}N_2O_4$ requires N = 3·89 per cent.).

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[*] In the portion of this work relating to the interaction of benzil and benzylamine, the deducing of these somewhat complex formulæ from the results of analysis was, of course, greatly facilitated by the consideration that the number of carbon atoms in the molecule of any compound formed would almost certainly be some multiple of 7.

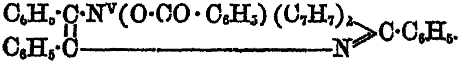
The obvious explanation of the formation of this compound during the recrystallisation of the hydroxide from benzene was that a portion of the hydroxide had been converted by aërial oxidation into benzoic acid, the latter substance then interacting with the unchanged hydroxide according to the foregoing equation. This view was readily tested. Into each of two tubes filled with and standing over mercury, 0·3 gram of the hydroxide was introduced, together with 15 c.c. of benzene, after which oxygen was passed into one of the tubes. After two days, 11 c.c. of oxygen had been absorbed; the yellow colour of the hydroxide had disappeared, and the liquid was filled with slender needles of the dibenzoate. The solution in the other tube was unchanged, except that it had deposited a mere trace of the needles, the formation of which was doubtless due to oxygen dissolved in the benzene employed.

The needles of the dibenzoate from benzene contain 1 mol. of benzene of crystallisation, but, owing to rapid efflorescence, an accurate determination could not be made. From alcohol it is deposited in transparent prisms containing 1 mol. of alcohol of crystallisation.

3·8246 lost 0·2465 at 100°. Alcohol = 6·44.

$C_{49}H_{40}N_2O_4,C_2H_5{\cdot}OH$ requires alcohol = 6·01 per cent.

As it was probable that the dibenzoate would readily part with its extra molecule of benzoic acid, we dissolved it in alcohol, added alcoholic ammonia, and then precipitated the organic substance by adding water. A colourless, crystalline powder separated; square, tabular crystals of the same substance were also deposited from the mother liquor on standing. It melted at 180°. A nitrogen determination, made with substance dried at 120°, gave figures agreeing with those required by the expected *dibenzyllophonium monobenzoate*,



$$\begin{array}{l} C_6H_5{\cdot}\overset{}{C}{\cdot}N^{V}(O{\cdot}CO{\cdot}C_6H_5)(C_7H_7)_2 \\ \quad\ \| \\ C_6H_5{\cdot}C\text{———————————}N \end{array}\!\!>\!C{\cdot}C_6H_5.$$

0·2843 gave 11·75 c.c. moist nitrogen at 8° and 741·5 mm. N = 4·87.

$C_{42}H_{34}N_2O_2$ requires N = 4·68 per cent.

Dibenzyllophonium Nitrate.—This compound was incidentally obtained in the determination of chlorine in dibenzyllophonium chloride. The chlorine was precipitated from an alcoholic solution of the chloride with silver nitrate. The filtrate, on standing, deposited magnificent, lustrous crystals of rhombohedral habit, melting with decomposition and evolution of gas at 208°. They left no residue on ignition. This substance, which was obviously the nitrate formed by double decomposition, was recrystallised, and its percentage of nitrogen determined.

0·1896 gave 12·0 c.c. moist nitrogen at 7·5° and 760·5 mm. N = 7·66.

$C_{35}H_{29}N_2{\cdot}NO_3$ requires N = 7·79 per cent.

2. *Benzil and Ethylamine.*

Four grams of benzil, 1·7 grams of ethylamine, dissolved in 5·5 c.c. of absolute alcohol, and 1·6 grams of finely-powdered zinc chloride were heated in a sealed tube for 5 hours at 120°. On cooling, the contents consisted of a dark pink liquid, with a white powder (zinc hydroxide).

The united product from several such tubes was dissolved in a smal quantity of alcohol with sufficient glacial acetic acid to dissolve the zinc hydroxide. Six volumes of ether were then added, which caused the separation of a viscous liquid. The supernatant ether was transferred to a separating globe, washed with water, preserving the aqueous liquid, and then shaken several times with very dilute hydrochloric acid. If the acid was too strong, a turbidity was occasioned, due to the insolubility of the hydrochloride of the new base in excess of hydrochloric acid; this disappeared on addition of water. The hydrochloric acid extracts were evaporated to dryness, and the syrupy residue treated with water, in which it all dissolved, excepting a small quantity of brown substance, which proved to be impure benzil. The clear aqueous solution was precipitated with ammonia and the liberated organic base extracted with ether. On evaporating the ether to a small bulk and allowing it to stand, the base crystallised with some difficulty. It was recrystallised from ether, and afterwards from light petroleum, which deposited it in large, lustrous prisms, melting constantly at 125·5°. A further quantity was obtained on addition of ammonia to the aqueous washings of the ether. The total yield from 24 grams of benzil was only about 2 grams. Analysis gave figures agreeing with the formula $C_{18}H_{18}N_2$.

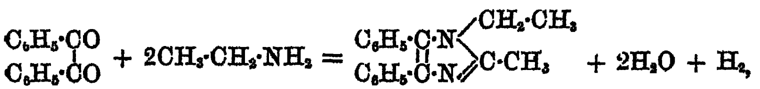
0·1225 gave 0·3700 CO_2 and 0·0764 H_2O. C = 82·38; H = 6·93.

0·2343 „ 20·6 c.c. moist nitrogen at 10·5° and 772·5 mm. N = 10·67.

$C_{18}H_{18}N_2$ requires C = 82·44; H = 6·87; N = 10·69 per cent.

The same compound is obtained when benzil and ethylamine are heated in alcoholic solution without the addition of zinc chloride but the yield is even less satisfactory.

The formation of the compound is represented by the equation



$$\begin{array}{l}C_6H_5\cdot CO\\ \quad\;|\\ C_6H_5\cdot CO\end{array} + 2CH_3\cdot CH_2\cdot NH_2 = \begin{array}{l}C_6H_5\cdot C\cdot N\diagup CH_2\cdot CH_3\\ \qquad\;\;\|\qquad\quad\rangle C\cdot CH_3\\ C_6H_5\cdot C\cdot N\diagup\end{array} + 2H_2O + H_2,$$

and it has thus the constitution, as we shall prove by a separate synthesis, of *N-ethyl-diphenyl-μ-methyl-imidazole.*

The hydrochloride is readily soluble both in water and in alcohol; but the salt is precipitated from the aqueous solution by excess of hydrochloric acid. On adding platinic chloride to the aqueous solution the platinichloride was deposited in well-formed, rhomboidal crystals. It was dried at 80° and analysed.

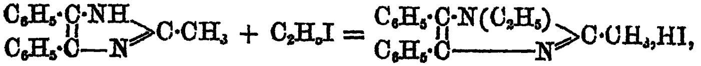
0·5581 gave 0·1168 platinum. Pt = 20·93.
$(C_{18}H_{18}N_2)_2H_2PtCl_6$ requires Pt = 20·84 per cent.

The viscous liquid, precipitated by ether in the treatment of the original product of the benzil ethylamine interaction, would contain, along with zinc chloride and zinc acetate, the zinc double salt of any quaternary chloride that had been formed. By dissolving it in water, removing the zinc with ammonium sulphide, evaporating the filtrate to dryness, extracting the residue with absolute alcohol, and again evaporating the alcoholic solution, a syrupy substance was obtained, which, from its reactions, was probably the quaternary chloride in question; but as we failed to obtain it in a crystallised form, we did not investigate it further. The difficulties which we afterwards experienced with the corresponding quaternary iodide, prepared by the union of the tertiary base with ethylic iodide, sufficiently explain our failure.

Synthesis of N-Ethyl-diphenyl-μ-methyl-imidazole from Diphenyl-μ-methyl-imidazole and Ethylic Iodide.—3 grams of diphenyl-μ-methyl-imidazole, prepared by the interaction of benzil, aldehyde and ammonia (Japp and Wynne, Trans., 1886, **49**, 464), were heated with excess of ethylic iodide in a sealed tube for 6 hours at 100°. The contents of the tube, consisting of a mass of brown crystals, were removed from the tube with alcohol, evaporated to dryness, dissolved in hot water, and the solution filtered. Ammonia precipitated an oily base, which, in contact with a crystal of the base $C_{18}H_{18}N_2$, obtained in the previous interaction, solidified. It was recrystallised from hot light petroleum, in which it all dissolved, excepting a small residue; this proved to be unchanged diphenyl-μ-methyl-imidazole. The solution deposited prisms melting at 125·5°, in every respect identical with those of the base $C_{18}H_{18}N_2$, with which formula a nitrogen determination also agreed.

0·1129 gave 10·3 c.c. moist nitrogen at 9° and 746·5 mm. N = 10·70.
$C_{18}H_{16}N_2$ requires N = 10·69 per cent.

It is formed according to the equation



$$\begin{matrix} C_6H_5\cdot C\cdot NH \\ \| \\ C_6H_5\cdot C - N \end{matrix}\!\!>\!C\cdot CH_3 + C_2H_5I = \begin{matrix} C_6H_5\cdot C\cdot N(C_2H_5) \\ \| \\ C_6H_5\cdot C \text{———} N \end{matrix}\!\!>\!C\cdot CH_3,HI,$$

thus proving it to be N-ethyl-diphenyl-μ-methyl-imidazole.

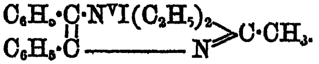
N-Diethyl-diphenyl-μ-methyl-imidazolonium Iodide.—This compound was prepared in order to obtain fresh proof of the tertiary nature of the base $C_{18}H_{18}N_2$.

One gram of the base $C_{18}H_{18}N_2$ was heated with excess of ethylic iodide in a sealed tube at 100—110° for four hours. The tube contained clear, well-shaped crystals of the new compound; these were removed with alcohol, and the solution evaporated to dryness. It was found impossible to obtain the compound in a crystallised form from any solvent. It was dissolved in water, in which it is only sparingly soluble, and the filtered solution was allowed to evaporate over sulphuric acid in a vacuum desiccator. It separated as an oil. When the water was all gone, this oil was heated on the water bath, and stirred with a glass rod, which had the desired effect of making it assume a crystalline form. Although the crystals melted as high as 163°, mere contact with ether, in which they are practically insoluble, caused them to liquefy. For analysis they were dried at 120—130°.

1·0351 gave 0·5816 AgI. I = 30·35.

$C_{20}H_{23}N_2I$ requires I = 30·32 per cent.

Its constitution is represented by the formula



$$\begin{array}{l} C_6H_5\cdot C\cdot N^{VI}I(C_2H_5)_2 \\ \qquad \| \\ C_6H_5\cdot C \text{———————} N \end{array} > C\cdot CH_3.$$

3. *Phenanthraquinone and Methylamine.*

Eight grams of phenanthraquinone and 2·5 grams of methylamine, the latter being dissolved in 12 grams of absolute alcohol, were heated in a sealed tube for six hours at 90—95°. The tube, on cooling, contained a brown liquid with a small quantity of a brown solid. The whole was treated with hot alcohol, which dissolved everything except about two grams of solid substance. The alcoholic solution, on standing, deposited a small quantity of a yellowish-brown substance, which was removed by filtration, evidently the sparingly soluble compound described by Zincke and Hof (*loc. cit.*); but we did not trouble further about this compound, as it was the readily soluble base which we wished to examine. To the alcoholic filtrate hydrochloric acid was added; the liquid was evaporated to a small bulk, and then extracted with water. On adding ammonia to the aqueous extract, the organic base was precipitated as a brown powder. Following Zincke and Hof's directions, we recrystallised the compound from alcohol, but, finding that this did not readily remove the colour, we employed light petroleum as a solvent, and thus obtained the base in colourless needles melting at 188° (185—186°, according to Zincke and Hof). Analysis gave figures pointing to the formula $C_{16}H_{12}N_2$, which contains two atoms of hydrogen fewer than that given by Zincke and Hof.

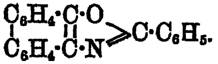
0·1373 gave 0·4165 CO_2 and 0·0639 H_2O; C = 82·73; H = 5·17
0·1375 „ 0·4174 CO_2 and 0·0659 H_2O, C = 82·79; H = 5·33
0·1292 „ 13·15 c.c. moist nitrogen at 9° and 752·5 mm N = 12·12.
$C_{16}H_{12}N_2$ requires C = 82·76; H = 5·17; N = 12·07 per cent.

Zincke and Hof's formula, $C_{16}H_{14}N_2$, on the other hand, requires C = 82·05; H = 5·98; N = 11·97 per cent. As already mentioned, no analyses are given in their paper.

The constitution of an *N-methyl-diphenylene-imidazole*, which we incline to assign to this compound, is given in the Introduction to the present paper. Since, according to this view, the compound is a tertiary amine, it ought to combine with alkyl haloids. We accordingly heated it with methylic iodide and methylic alcohol in a sealed tube, and obtained a compound which crystallised from its aqueous solution in prisms, and was not precipitated by ammonia; but as at each recrystallisation this substance became in part reddish-brown and insoluble, apparently from oxidation, we did not examine it further.

4. *Phenanthraquinone and Benzylamine.*

Four grams of phenanthraquinone were rubbed in a mortar with 1·5 gram of zinc chloride. The mixture, which was of a dark reddish-brown colour, owing to the formation of the double compound of these two substances, was transferred to a large boiling tube, and 4 grams of benzylamine were added. Immediately there was an effervescence, with evolution of heat, and the colour changed to dark blue. The mixture was heated on the water bath, but as no change was observed, it was transferred to an oil bath, and the temperature gradually raised, first to 120° and ultimately to 150°. The effervescence increased, lasting for a few minutes, and ammonia was given off. The heating was continued for half an hour. The mass on cooling was hard, and of a dull yellow colour. It was powdered and then extracted with boiling alcohol, which dissolved but a small proportion. The alcoholic solution, on standing, deposited needle-shaped crystals with a silky lustre; these were recrystallised from benzene, when they melted at 197°. From the melting point, appearance, ready solubility in benzene, and sparing solubility in alcohol or glacial acetic acid, it was evidently identical with *diphenylene-μ-phenyloxazole*,



$$\begin{array}{l} C_6H_4\cdot C\cdot O \\ \,| \quad\;\; \| \\ C_6H_4\cdot C\cdot N \end{array} \!\!\geqslant C\cdot C_6H_5.$$

The latter compound, it is true, melts at 202°; but this melting point can be observed only with colourless substance, and after repeated recrystallisation; whereas the present specimen had a yellowish tinge, and the quantity was insufficient for further purification. It was, therefore, identified by careful comparison with a specimen of diphenylene-μ-phenyloxazole prepared from phenanthraquinone, benzaldehyde, and ammonia. Except as regards the slight, yellowish tinge, and the fact that it melted 2° lower, it was indistinguishable from this specimen. Finally, a nitrogen determination gave a value agreeing with that required by the formula.

0·1988 gave 8 c.c. moist nitrogen at 8° and 742 mm.; N = 4·74.
$C_{21}H_{13}NO$ requires N = 4·74 per cent.

The substance which remained after extracting with boiling alcohol was found to be insoluble in the ordinary organic solvents of low boiling point. It could be recrystallised, however, from boiling aniline, from which it was deposited in microscopic, brownish, rectangular prisms, with a bronze lustre. It was twice crystallised from this solvent, washed with alcohol, and dried for analysis. It did not melt below 300°, and could not be sublimed. When dissolved in cold concentrated sulphuric acid, it gave a very faint bluish colour; but the liquid, on warming on the water bath, became of an intense blue colour, and this solution, when diluted with water, dyed silk greenish-blue; the colour fading, however, in a few days. Two combustions of different preparations, together with a nitrogen determination, were made; but the figures were not very concordant: C = 87·28—88·00; H = 4·58—5·01; N = 3·94. The nearest to this is the formula $C_{28}H_{17}NO$, which requires C = 87·72; H = 4·44; N = 3·66 per cent. The substance was difficult to burn.

On adding alcohol to the aniline mother liquor from the first of the foregoing crystallisations, microscopic, yellowish, rhomboidal plates were precipitated. These proved to be tetraphenyleneazine, $C_{28}H_{16}N_2$. It dissolved in cold concentrated sulphuric acid, with the characteristic, intense blue colour, which disappears on addition of water. So far as we are aware, tetraphenyleneazine has not hitherto, on account of its sparing solubility, been obtained crystallised from any solvent; it has been usual to purify it by sublimation.

Other experiments were made on the interaction of phenanthraquinone and benzylamine without the addition of zinc chloride; but the same products were obtained as in the previous case.

Chemical Department,
University of Aberdeen.

VI.—*A New Method of obtaining Dihydroxytartaric acid, and the use of this acid as a Reagent for Sodium.*

By H. J. H. Fenton, M.A.

An account was given in a former paper (Trans., 1894, **65**, 899) of a new acid having the formula $C_4H_4O_6,2H_2O$, which is obtained by the oxidation of tartaric acid in presence of iron. Experiments illustrating the constitution of this acid are now in progress, and I hope shortly to communicate their results to the Society.

The composition of this acid shows that it is closely related to tartaric acid and to dihydroxytartaric acid; the crystallised acid, $C_4H_8O_8$, containing two atoms of hydrogen more than dihydroxytartaric acid, and the anhydrous acid, $C_4H_4O_6$, containing two atoms of hydrogen less than tartaric acid. It seemed probable, from this relation, that the new acid should yield dihydroxytartaric acid as a product of oxidation, and experiments show that this change may be readily effected.

Aqueous solutions of various oxidising agents such as hydrogen dioxide, nitric acid, potassium permanganate, chlorine or bromine, gave negative or unsatisfactory results; but if the proportion of water be kept at the minimum necessary to complete the change, chlorine or bromine are found to give a considerable yield of dihydroxytartaric acid. Performed in the following manner, the change seems to take place quantitatively according to the equation,

$$C_4H_4O_6,2H_2O + Br_2 = C_4H_6O_8 + 2HBr.$$

The crystallised acid is covered with glacial acetic acid, and a solution of bromine in glacial acetic acid is added drop by drop with constant shaking. The first portions of bromine added are almost instantly decolorised, copious fumes of hydrogen bromide being evolved. As the action proceeds it is necessary to add, gradually, a few drops of water to complete the change. The addition of bromine is continued until a faint, permanent, yellow colour is just visible. Complete solution results when this stage is arrived at, the original acid being almost insoluble in cold glacial acetic acid.

Using standard solutions of bromine and weighed quantities of the crystallised acid, the following results were obtained.

I. 0·7023 gram of the acid required 5 c.c. of bromine solution containing 0·1246 gram of bromine per c.c., = 0·6230 gram Br.
Theory = 0·6106 gram Br = 4·9 c.c.

II. 0·9933 gram of the acid required 3·95 c.c. of bromine solution containing 0·21019 gram of bromine per c.c., = 0·83025 gram Br.
Theory = 0·8637 gram Br = 4·10 c.c.

On neutralising with sodium carbonate the liquid thus obtained, a heavy, white, crystalline precipitate was immediately produced. This was collected, washed several times with cold water, drained with the aid of the pump, dried in a vacuum over sulphuric acid, and analysed.

III. 0·8987 gave 0·4612 Na_2SO_4; Na = 16 62.
IV. 0·6167 „ 0·3164 Na_2SO_4; Na = 16·61.
V. 0·5891 „ 0·3074 Na_2SO_4; Na = 16·90.

Kekulé (*Annalen*, **221**, 253) obtained the following numbers on analysis of sodium dihydroxytartrate prepared from "nitrotartaric" acid and from pyrocatechin,

17 23, 17·02, 17·39, 17·04, 16·91, 16·79, 16·82 per cent. Na.
Theory for $C_4H_4Na_2O_8 2\frac{1}{2}H_2O$ = 16·79 per cent. Na.

The yield of sodium salt obtained by the above method does not fall far short of the theoretical. Thus the result of Experiment I. when treated in the manner described, gave 0·9478 gram sodium salt dried in a vacuum. Theory = 1·0343 gram.

The acid was obtained from this salt by Miller's method (*Ber.*, 1889, 2015); that is, the salt was covered with anhydrous ether and dry hydrogen chloride passed into the mixture, care being taken to avoid excess; the ethereal solution was then evaporated over sulphuric acid in a vacuum, and the syrupy residue slowly crystallised, or, if only small quantities were worked on, white crystals generally appeared as the liquid evaporated. These crystals exhibit all the properties of dihydroxytartaric acid. They melt and decompose at 98°, and are very easily soluble in cold water; the aqueous solution gives an immediate white, crystalline precipitate with sodium carbonate, whilst with phenylhydrazine hydrochloride, on warming, it gives the characteristic orange precipitate of the "osazone;" the latter, when dried, melted at 102—104°.

For analysis, the crystals of the acid were washed with anhydrous ether and kept in a vacuum over sulphuric acid. The numbers obtained agreed almost exactly with those required by theory.

0·1742 gave 0·1685 CO_2 and 0·0514 H_2O; C = 26·38; H = 3·27.
$C_4H_6O_8$ requires C = 26·37. H = 3·30 per cent.

Considering the ease with which it is possible to prepare dihydroxytartaric acid by the above method, I would suggest the use of this acid as a reagent for the detection of sodium. A few crystals of the acid are dissolved in a drop of water on a watch glass, the solution to be examined is added, and the liquid neutralised, if necessary, with a drop of ammonia. On stirring with a rod, the white crystalline precipitate appears, usually in lines, as in the detection of potassium by tartaric acid or by platinic chloride. The test is fairly delicate, a 1 per cent. solution of sodium chloride giving the reaction almost immediately, and weaker solutions after some minutes. Potassium and ammonium salts do not seem to interfere with the action.

It might perhaps be possible to estimate sodium quantitatively by this method if a correction were made for the slight solubility of sodium dihydroxytartrate in water. This substance appears to be much less soluble in salt solutions than in pure water, since a turbidity is always produced when, in the preparation above described, the final washings run into the filtrate. If the pure salt be shaken with water and the liquid filtered into a strong solution of sodium chloride, a turbidity appears almost immediately.

Later experiments have shown that, in order to obtain free dihydroxytartaric acid it is not necessary first to prepare the sodium salt. If the acetic acid solution, obtained in the manner above described, be kept in a vacuum over solid potash, crystals of the acid are deposited as the solution becomes more concentrated. These may be drained off and washed with small quantities of ether. The acid prepared in this way is perhaps less pure than that obtained from the sodium salt, but it answers perfectly well for analytical purposes.

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Cambridge.

VII.—*Isomeric Dinitrodiazoamidobenzenes and their Melting points.*

By R. Meldola, F.R.S., and F. W. Streatfeild, F.I.C.

The melting point of paradinitrodiazoamidobenzene,

$$(p)NO_2 \cdot C_6H_4 \cdot N_3H \cdot C_6H_4 \cdot NO_2(p),$$

was given by its discoverer, Griess, as 224·5° (*Annalen*, **121**, 271). Subsequently we gave the melting point as 223° (Trans., 1886, **49**, 627), stating that at this temperature it also underwent decomposition. In a later communication, we pointed out that the decomposing point was very much under control, as, by running up the temperature rapidly, we succeeded in raising it to 228° (Trans., 1889, **55**, 416). During the present year, the compound in question has again been brought under the notice of chemists, first by Pawlewski (*Ber.*, 1894, **27**, 1565) and subsequently by Bamberger (*ibid.*, 1952). The first of these observers gives the melting point as 231°, and the latter as 233°, or 231° when the temperature was raised very slowly. Although the determination of the melting points of easily decomposable compounds within a few degrees in either direction is not, under ordinary circumstances, a matter of particular importance, in the present case it seemed desirable to reinvestigate the matter, in view of the possible existence of stereoisomeric diazoamido-compounds (Hantzsch, *Ber.*, 1894, **27**, 1857; compare Bamberger, *ibid.*, 2596; Hantzsch, *ibid.*, 2968; and also the authors, in Trans., 1890, **57**, 807).

A specimen of the diparadinitro-compound prepared by us for our former investigations, was crystallised repeatedly from methylic alcohol till the melting point was constant. The melting point of this preparation was then observed by ourselves and students under various conditions. The accuracy of the thermometer was first ascertained by comparison with other standard thermometers. Without giving all the determinations, we may state, as a final result, that, according to our observations, the compound has no true melting point, but a point of decomposition, which ranges from 220° to about 236°, according to the rate at which the temperature is raised. We use the ordinary method with a small beaker of strong sulphuric acid, and no correction has been applied for the portion of the thermometer stem out of the bath. If this correction is applied, 6° must be added to the temperatures given, but, as the other observers make no specific statement to the contrary, we presume their melting points are also uncorrected. In order to give some definiteness to the expression "rate at which the temperature is raised," we may add that in the slowest observations the temperature was raised about 1° in 15 seconds, and in the quickest observations about 1° in 3 seconds, the readings being timed from 200° upwards.

Having familiarised ourselves with the behaviour of the compound on heating, we applied to Dr. Pawlewski and to Dr. Bamberger for specimens of their products, as these had been obtained by methods differing from ours, more especially in the absence of strong mineral acids, and we desired to compare the various preparations. Both the chemists named very kindly forwarded specimens, and we are glad of the present opportunity of acknowledging their courtesy. A comparison of the products showed that they possessed the same latitude of decomposing point and were identical with ours in every other respect.

In the paper by Pawlewski above referred to, this author assigns as a reason for believing that 231° is the true melting point of the diparadinitrodiazoamide, the similarity in the difference between the melting points of the dipara- and the dimetadinitro-compounds and the corresponding nitranilines. He makes this difference 84°, but this result is arrived at by taking the melting point of metanitraniline as 110°, a statement for which Körner appears to be the authority. Hübner, however, found the melting point to be 114°, and a careful series of determinations by ourselves gave the melting point as 113° (uncorr.). Taking the melting point of the dimetadinitro-compound as 194°, the difference should therefore be 81°, and the melting point of the dipara-compound = m. p. of paranitraniline + 81° = 228°, and not 231° as given by Pawlewski.

In order to complete the set of isomerides, the hitherto undescribed diortho-compound, $(o)NO_2{\cdot}C_6H_4{\cdot}N_3H{\cdot}C_6H_4{\cdot}NO_2(o)$, was prepared by diazotising orthonitraniline in cold glacial acetic acid solution with the calculated quantity of sodium nitrite added in small portions in the solid state. The compound separates in a crystalline form in a few hours. It is best to work in a strong, that is, cold saturated solution, and to add the nitrite very slowly, in the manner described. The yield is not so good as in the case of the dimeta- and diparadinitro-compounds, as a considerable quantity of some resinous substance is formed as a bye-product and remains dissolved in the mother liquor. It may be of interest to add that the diortho-compound cannot be prepared in aqueous or alcoholic solution by any of the usual methods, but it is possible that a better yield than is given by our method would be obtained by diazotising with an alkylic nitrite in some neutral solvent, such as ethylic acetate. We actually obtained about 1·7 grams of the pure substance from 5 grams of orthonitraniline. The compound has the following properties: although it dissolves but sparingly in boiling alcohol, it can be advantageously crystallised from this solvent. It separates in yellow needles from a small quantity of the solution in a test-tube, whilst from a large volume of the solution, allowed to cool slowly, it separates in the form of beautiful, golden scales. It melts at 196—196·5° without undergoing decomposition; the difference between this and the melting point of orthonitraniline (72°) is 124°, and Pawlowski's rule evidently fails. The analysis of our compound showed that it had the composition of a dinitrodiazoamide.

0·0986 gave 20·4 c.c. moist nitrogen at 15·5° and 767·2 mm. N = 24·37.
The formula requires N = 24·39 per cent.

As the melting point of the compound was so widely divergent from that calculated by Pawlewski's rule (72° + 81° = 153°), we made experiments with the special object of ascertaining whether it might not have been the metameric amidoazo-compound. All the properties, however, agreed with those of a true diazoamide. When heated in a dry tube, the substance explodes with deflagration, leaving a carbonaceous residue. It is more stable towards acids than the isomeric dimeta- and dipara-compounds, as it can be allowed to stand for days under strong hydrochloric acid at ordinary temperatures without undergoing any change. When boiled with dilute sulphuric acid (1 volume of strong acid to 2 of water), it decomposes with evolution of nitrogen, and the formation of orthonitraniline. Heated in a sealed tube with strong hydrochloric acid, it decomposes completely at 100° in three or four hours, the products being orthonitrochlorobenzene, orthonitraniline, and nitrogen. The decomposition is perfectly analogous to that which the isomerides undergo under similar conditions (Trans., 1886, **49**, 629).

The foregoing results furnish fairly good evidence for the diazo-constitution, but the acid character of the compound appears to us to establish this constitution beyond question. It dissolves in cold alcoholic or boiling aqueous caustic soda with a reddish-brown colour, the sodium salt separating out in the form of bronzy needles. We have satisfied ourselves that this crystalline deposit is a salt, and not a product of reduction, because it gives the unaltered diazoamide on treatment with acids (see Pawlewski, *Ber.*, 1894, **27**, 1566; also the authors, *ibid.*, 2202). Although the compound is acid enough to form salts, the latter are somewhat unstable, and lose their alkali metal on washing with water, the decomposition being indicated by a change of colour from bronzy to orange, and the unchanged diazo-compound being left on the filter. For this reason, it has not been possible to make a satisfactory analysis of the potassium or sodium salt. Even the silver salt, which was prepared by adding ammoniacal silver nitrate to a hot solution of the diazo-compound in alcoholic ammonia, and which consists of brown needles, appears to undergo partial decomposition on washing with alcoholic ammonia.

0·1452 gave 0·0382 Ag. Ag = 26·31.
The formula $NO_2{\cdot}C_6H_4{\cdot}N_3Ag{\cdot}C_6H_4{\cdot}NO_2$ requires Ag = 27·41 per cent.

The compound does not appear to be alkylised with the same readiness as its isomerides. We have tried the action of ethylic iodide on the potassium and on the silver salts, but under the same conditions as those which enabled us to prepare the ethylic salts of the isomerides with such facility the present compound remained unaltered. We have not studied the action of reducing agents on the compound, as Pawlewski is following up this branch of the work, which was commenced by us in a former paper (Trans., 1886, **49**, 628), and as this author has obtained results which promise to be of interest, we leave him in possession of the field. We have only to point out that the majority of the new products of reduction described by Pawlewski are amorphous, and that the constitutional formulæ assigned are based solely upon the analytical results, without any other evidence being adduced (*Ber.*, 1894, **27**, 1565).

It gives us much pleasure to acknowledge the assistance which has been given in the course of the work by two of our students, Messrs. H. W. Younger and E. R. Andrews.

VIII.—*Essential Oil of Hops.*

By Alfred C. Chapman.

The essential oil of hops has been submitted to investigation at different times by several chemists who, according to their published statements, obtained from it terpenes boiling at 160° and 175°, and an oxidised constituent to which the formula $C_{10}H_{16}O$ (or $C_{10}H_{18}O$) has been assigned, but which does not appear to have been isolated in a state of purity.

Payen and Chevallier examined the oil in 1822, and separated it into two fractions by distillation. Wagner, in 1853, obtained a terpene boiling at 175° and an oxygenated compound which yielded valeric acid on oxidation. Personne, in an admirable paper entitled "Histoire chimique et naturelle de lupulin" (*J. Pharm.*, [3], **26**, 241, 329 ; **27**, 22), obtained a fraction, boiling between 150—160°, of a light yellow colour, and sp. gr. of 0·8887. It rotated a ray of polarised light 2·7° to the right in a tube 80 mm. long. When acted on by fused caustic potash, potassic valerate was formed and hydrogen evolved.

The essential oil of hops has also been examined by J. Ossipow (*J. Pr. Chem.*, [2], **28**, 448), who paid particular attention to the products obtained on oxidising the oil by means of chromic mixture. In his first paper, entitled "Vorlaüfige Notiz über das Hopfenöl aus käuflichem Lupulin," published in 1883, he refers to the action of bromine, and of chromic mixture on the oil, and in his second paper, published in 1886, he practically confines his attention to the fractionation of the volatile acids obtained on its oxidation. Of these acids, he was able to identify acetic acid and isovaleric acid. These various researches, however, throw but little light on the real nature of the constituents of this essential oil.

The important researches of Wallach and others on the terpenes and essential oils has enormously enlarged our knowledge of these substances during the last few years, and the investigation described in this paper was undertaken with the object of studying the essential oil of hops in the light of this extended knowledge. In a preliminary notice communicated to the Society (Proc., 1893, 177) I published an account of a partial examination of one sample of oil, and briefly described a sesquiterpene obtained from it by fractional distillation. Since then I have submitted to examination three other samples of the oil, and have obtained results of a more definite character. Owing to unexpected difficulties in connection with two of the constituents, I have not as yet been able to complete the investigation, but having obtained a large quantity of the oil, I hope to be able to examine these constituents more thoroughly.

In this research I have examined four samples of the essential oil, which will be referred to as Nos. 1, 2, 3, and 4 respectively.

Sample No. 1.—This sample I prepared myself by the steam distillation of about 80 kilos. of hops, some of which had been grown in Burgundy, some in Alsace, and the remainder in Kent and Sussex. The oil so obtained was twice distilled over water to free it from resin, and was dried over chloride of calcium and anhydrous sodium sulphate. About 140 c.c. of nearly colourless oil was finally obtained.

Sample No. 2.—This sample I obtained through the kindness of Messrs. Wright, Layman, and Umney, of Southwark. It had been distilled in May, 1893, from German hops of 1892 growth, by Messrs. Schimmel and Co., of Leipzig, and was guaranteed genuine by that firm. The oil was of a pale yellow colour and perfectly bright.

Sample No. 3.—This was the largest sample with which I worked. For it I am indebted to Messrs. Schimmel and Co., of Leipzig, who kindly distilled it for me from the best Bavarian hops of 1893 growth.

Sample No. 4.—This sample I prepared myself by the steam distillation of about 100 kilos. of English and foreign hops of 1894 growth, obtaining about 150 c.c. of the purified and dried oil.

Of the genuineness of all these samples, therefore, there can be no doubt whatever.

The above four samples of oil had the following relative densities and specific rotatory powers.

	d 15°/15°.	*d* 20°/20°.	$[\alpha]_D$.*
No. 1........	0·8802	0·8776	+0·41°
No. 2........	0·8662	0·8636	+0·58°
No. 3........	0·8771	0·8739	+0·50°
No. 4........	0·8743	0·8716	—

All of these samples were neutral to litmus, and free from sulphur. On cooling to −20° they became more viscous, but did not yield any crystalline substance. The oil dissolved in cold concentrated sulphuric acid, giving a blood-red solution, from which water precipitated a reddish oil, having a smell somewhat resembling that of valeric acid. Shaken up with a saturated solution of sodium hydrogen sulphite, the oil gave no crystalline compound, and there was no noticeable development of heat. On shaking with a strong solution of caustic potash, it experienced no appreciable diminution of volume, and it did not reduce an ammoniacal solution of silver nitrate.

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* The determinations of circular rotation mentioned in this paper were made with a Laurent instrument, using sodium light.

Fractionation of the Oil.

The first sample of oil was distilled under atmospheric pressure. It commenced to boil at 170°, but the temperature rose rapidly to 230°, and the greater part of the oil distilled over between 230° and 270°. After several fractionations three fractions were obtained, the first boiling at 170—255°, the second (corresponding to about four-fifths of the whole oil) at 255—260°, and a third small fraction at 260—270°. The first and third fractions were very small. The second fraction, after purification by distillation over sodium, was found to consist of a sesquiterpene, which is described fully in this paper, and which has also been obtained in considerable quantity from all the other three samples.

The three samples (representing the great bulk of the oil with which I worked) were fractionally distilled under a pressure of 60 mm., a current of carbon dioxide being passed into the liquid to ensure regular ebullition; each sample was distilled separately, the fractions of corresponding boiling points obtained from the different samples being mixed after their identity had been ascertained.

After prolonged fractionation under these conditions, the following fractions were obtained.

(1) 89—91° (2) 145—150°
(3) 163—168° (4) 168—173°

Nos. 1 and 4 were the main fractions, the remaining two being small. No. 4 fraction corresponded to nearly two-thirds of the oil used.

Fraction No. 1 (b. p. 89—91°).—This was a colourless, very mobile liquid, of characteristic smell. When boiled with a small piece of sodium, it was found to be practically unacted on, and, on analysis, was found to consist almost entirely of carbon and hydrogen. It was purified by repeated distillation over sodium under a pressure of 50 mm. until the metal remained bright to the end of the operation; thus purified, it boiled at 86—89° (50 mm.), and further fractionation failed to split it up into two distinct fractions.

The greater part of this liquid boiled between 166° and 171° under atmospheric pressure, but towards the end the boiling point suddenly rose to about 250°; on stopping the distillation, a small quantity of a yellowish, viscous oil remained in the flask. On continuing the distillation of this viscous oil, the thermometer rose to 320°, and a solid resin remained. A portion of this fraction, therefore, undergoes polymerisation, and oxidation change, when boiled under ordinary atmospheric pressure. On exposure to the air, it absorbs oxygen with great rapidity, becoming first very viscous and ultimately changing into a colourless, hard resin. I found *d* 20°/20° = 0·799.

Being extremely surprised at this low number, I made many density determinations of the corresponding fractions obtained from all three samples of oil, and found in all cases almost identical numbers, namely, 0·798, 0·797, and 0·799.

When examined in a tube 100 mm. long, at 15°, it produced a rotation of 0·56° to the left. It has, therefore, practically no action on polarised light.

On combustion, it gave the following numbers as the mean of two experiments which were in close agreement.

	Found.	Calculated for $C_{10}H_{17}$.
C........	87·75	87·59
H........	12·30	12·41

It will be seen that the carbon is lower (and the hydrogen, of course, proportionately higher) than would be required for a terpene or mixture of terpenes. The formula, $C_{10}H_{16}$, requires C = 88·23, H = 11·77. The differences are greater than can be accounted for by experimental error, more than ordinary care having been taken to ensure the accuracy of the hydrogen determinations.

A vapour density determination, by Hofmann's method, in toluene vapour (b. p. 111°), gave 5·0, $C_{10}H_{17}$ requiring 4·75.

On passing hydrogen chloride into a cooled solution of the liquid in ether, the gas was readily absorbed, and, when saturated, the solution was reddish-purple. The yellow oil left on evaporation of the ether, after having been kept for some days in a desiccator over caustic potash, was submitted to distillation under a pressure of 40 mm. Between 95° and 110° a colourless mobile oil distilled over containing 30·5 per cent. HCl. A dihydrochloride of the formula $C_{10}H_{16},2HCl$ requires 34·9 per cent. HCl. This result points either to a decomposition of the compound or (which is more probable in view of the other ascertained facts) to the liquid being a mixture of two distinct hydrochlorides. The quantity was too small to distil fractionally with any chance of success.

On adding bromine or a solution of bromine in chloroform, drop by drop, to a well-cooled solution of this fraction in ether or chloroform, the colour disappeared immediately at first, but when 3 to 4 atoms of bromine had been added for every molecule of the substance, it remained permanently coloured. Up to this point, there was practically no disengagement of hydrogen bromide, and, on allowing the solvent to evaporate, a dense yellow oil was left; this could not be obtained in a crystalline condition. When this oil was treated with aniline, action occurred at once, the mixture became very hot, and aniline hydrobromide separated. On adding hydrochloric acid and distilling with steam, no volatile hydrocarbon passed over, but a resinous mass remained in the distilling flask. The removal of hydrogen bromide in this way is therefore accompanied by the polymerisation of the original hydrocarbons.

Many attempts were made by well-known methods to prepare a nitrosochloride, but, although nitrosyl chloride was readily absorbed, no crystalline compound could be obtained. Attempts to prepare a nitrosite and a nitrosate were equally unsuccessful.

In the next place, the action of oxidizing agents on this fraction was investigated. A cold aqueous solution of potassium permanganate, containing 40 grams of the salt per litre, was added little by little to 3 grams of the oil. At first the colour of the permanganate disappeared at once, then somewhat more slowly, and finally remained tolerably permanent when an amount of the solution equivalent to 21 grams of the salt had been added. In this solution, carbonic acid, acetic acid, and oxalic acid were easily recognised. There was also present a very small quantity of some volatile acid having an odour resembling that of valeric acid. The oxalic acid was identified by its calcium salt, which was analysed. Boiling with dilute nitric acid of various strengths was also tried, but in all the experiments the only solid oxidation product which could be recognised with certainty was oxalic acid, the acid crystallising fairly readily from the different liquids after concentration. No evidence of the formation of any terephthalic acid was obtained The low specific gravity of this fraction and the impossibility of obtaining any crystalline compounds from it show that it is not any of the well-known terpenes. These terpenes have relative densities varying between 0·84 and 0·86 at 20°; this fraction is 0·799 at that temperature. It seems extremely probable, judging from the experimental results, that this fraction consists of two hydrocarbons, one having the formula $C_{10}H_{16}$ and the other $C_{10}H_{18}$. The latter is probably tetrahydrocymene (b. p. 167°), whilst the former may possibly be one of the "olefinic terpenes" described by Semmler (*Ber*, 1891, **24**, 682). So little, however, is known at present of the latter that until more work has been done in connection with them, it will be impossible to arrive at more definite conclusions. One thing, at least, is certain, the great bulk, if not the whole of the lower boiling point fraction of the essential oil of hops consists of hydrocarbons other than the ordinary terpenes. The general statement made in this connection by previous observers is to the effect that the lower fraction consists of "a terpene" boiling at about 170°. I may add that these hydrocarbons did not undergo any polymeric changes when sealed up in an exhausted tube and allowed to stand for six months at ordinary temperatures. At the time when this experimental work was done, I thought that I was the first to recognise the presence of a hydrocarbon of the formula $C_{10}H_{18}$ in an essential oil, but I have quite recently become acquainted with a paper by Andres and Andréeff (*Ber.*, 1892, **25**, 609) on Russian peppermint oil. In this paper, they state that the lower fractions of the oil consist of a mixture of two hydrocarbons, $C_{10}H_{16}$ and $C_{10}H_{18}$, and they consider the latter to be identical with the "dekanaphthylene" of Markownikoff and Ogloblin. They conclude by remarking, "Soweit uns bekannt, ist das der erste Fall, dass ein derartiger Kohlenwasserstoff in einem ätherischen Oele gefunden wird."

Fraction No. 2 (b. p. 145—150°).—Owing to the very small proportion in which this constituent occurred in all the samples of oil examined, I was unfortunately unable to obtain sufficient to permit of its satisfactory identification. The small fraction obtained was a colourless oil having a pleasant smell of oil of geranium with an after-smell of oil of rue. It did not solidify on being cooled to $-10°$. $d\ 15°/15° = 0·885$.

0·121 gave 0·348 CO_2 and 0·1275 H_2O. C = 78·43; H = 11·71.
$C_{10}H_{18}O$ requires C = 77·92; H = 11·69 per cent.

The compound unites readily with bromine, and in many of its properties appears to bear some resemblance to geraniol. I am now engaged in fractionating a large quantity of the essential oil and hope to be able ere long to complete the identification of this oxygenated constituent.

Fraction No. 3 (b. p. 163—168°) was a small fraction, having very little smell and containing 3·4 per cent. oxygen. It was found to consist of a mixture of the next higher fraction with a little of the fraction just described.

The Sesquiterpene.

Fraction No. 4 (*b. p.* 168—173°).—This fraction, which was by far the largest obtained, representing, in fact, nearly two-thirds of the whole of the oil used, was found to be identical with the fraction boiling between 256° and 261° (760 mm.), obtained from the first sample of oil, and of which a preliminary account has already been given to the Society. The substance was purified by repeated distillation over sodium under 60 mm. pressure, until the metal remained bright throughout the whole distillation. Thus purified, it boiled at 166—170° (60 mm.), and on combustion gave the following results.

I. 0·1065 gave 0·345 CO_2 and 0·1145 H_2O. C = 88·26; H = 11·92.
II. 0·1400 " 0·454 " " 0·1480 " C = 88·42; H = 11·71.
III. 0·1540 " 0·498 " " 0·1610 " C = 88·20; H = 11·69.
$C_{15}H_{24}$ requires C = 88·23; H = 11·77 per cent.

In determining its vapour density, it was found that Victor Meyer's method, using diphenylamine (b. p. 310°), did not give satisfactory results, since the vaporisation was very slow, and the substance underwent some decomposition. Two determinations, therefore, were made by Hofmann's method, using quinoline (b. p. 237°). The two results obtained were (1) 6·91 and (2) 7·1. The formula $C_{15}H_{24}$ requires 7·1. This fraction, therefore, consists of a sesquiterpene. The boiling point of this compound, corrected for the emergent mercurial column, is 263—266°. Its density determinations gave d 15°/15° = 0·9001, d 20°/20° = 0·8977.

The liquid when examined in a tube 100 mm. long, at 20°, produced a rotation of 0·5° to the left.

The sesquiterpene prepared from the first sample of essential oil (which was probably not quite so pure as this second and larger quantity) produced, under the same conditions, a rotation of 1·5° to the right. It is, therefore, evident that the sesquiterpene is optically inactive, the slight lævorotation observed in this case being due to a trace of some active impurity.

The following are the results of determinations of the index of refraction for the red hydrogen line and the sodium line (C and D).[*] The observations were made at 19°, and gave the values $\mu D = 1·5021$, and $\mu H\alpha = 1·4978$.

The specific refractive energy of the compound calculated by means of the $\dfrac{n^2 - 1}{(n^2 + 2)d}$ formula is, therefore, 0·3245, and the molecular refractive energy 66·2. Taking Brühl's numbers for the atomic refractions of carbon and hydrogen, the calculated number for $C_{15}H_{24} =_2$ is 65·7. This evidence of the presence of two pairs of "doubly linked" carbon atoms is borne out by the determinations of the amount of bromine with which one molecule of the sesquiterpene can directly combine, and by the preparation of a dihydrochloride described below.

Action of Bromine.—A solution of bromine in chloroform was run drop by drop into a solution of the sesquiterpene in five times its volume of the same solvent, kept cool by means of ice. The colour disappeared rapidly at first, and did not become permanent until 4 atoms of bromine had been added for every molecule of the compound present. At this stage, the evolution of hydrogen bromide, which had previously been slight, increased considerably. On allowing the chloroform to evaporate spontaneously, a viscous. yellow oil was left; it could not be induced to crystallise. Other experiments, using both chloroform and carbon bisulphide as solvents, showed that 1 molecule of the compound was capable of uniting directly with 4 atoms of bromine.

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[*] My best thanks are due to Mr. G. Finch, working in the Physical Laboratory of University College, London, for having been kind enough to make these determinations for me.

Action of Hydrogen Chloride.—Hydrogen chloride was passed to saturation into a well-cooled solution of the sesquiterpene in four times its volume of ether. The gas was readily absorbed, and the solution finally became purple. After allowing it to remain for some hours, and then evaporating the ether, a yellow oil was left; this, after being washed with small quantities of cold alcohol (in which it is somewhat soluble), was allowed to remain for several days in a vacuum over caustic potash and sulphuric acid. The clear yellow oil thus obtained, on being cooled to −15°, became more viscous, but did not show any tendency to crystallise even after the lapse of some hours. Distillation under reduced pressure (60 mm.) was then tried; at first there was a very considerable disengagement of gas, and then a colourless liquid distilled over between 165° and 185°. After two more distillations under the same pressure, the liquid boiled at 168—175°. A chlorine determination gave 3·7 per cent. HCl, $C_{15}H_{24},2HCl$ requiring 26·3 per cent. HCl. It is evident, therefore, that even under a pressure of 60 mm. this hydrochloride is almost completely decomposed, so that it is impossible to purify it by this means. Another quantity of the yellow oil, prepared and partially purified as above described, gave on analysis numbers approximately agreeing with those required by the formula $C_{15}H_{24},2HCl$. The relative density of this impure hydrochloride was 1·063 at 15°/15°.

On oxidation with cold aqueous solution of potassium permanganate, the sesquiterpene yielded considerable quantities of carbonic acid and acetic acid, together with a non-volatile acid, which could not be identified with certainty.

Action of Nitrosyl Chloride.—One volume of the sesquiterpene was dissolved in three volumes of chloroform, and the solution cooled in a freezing mixture to −15°; on passing nitrosyl chloride into it slowly, care being taken not to allow the temperature to rise, the liquid became green, and after a time a white crystalline substance separated, the quantity of which was increased when the product was poured into cold alcohol. The crystalline precipitate was quickly collected on a filter, washed with cold alcohol, and dried in a vacuum over sulphuric acid. The nitrosochloride obtained in this way is a white, finely crystalline substance, fairly soluble in chloroform; it can be obtained from this solution in a more distinctly crystalline condition by the addition of alcohol. Compared with the nitrosochlorides of the terpenes, it is very stable, since it can be heated to 140° without the slightest change of colour. At 164—165°, it melts to a brownish-black liquid, which then undergoes considerable decomposition. It was found to contain 12·90 per cent. chlorine instead of 13·16, the calculated amount.

When this nitrosochloride was heated with an excess of piperidine, almost to the boiling point of the latter, a vigorous action occurred resulting in the formation of a nitrolpiperide. Sufficient alcohol was added to completely dissolve the products formed, and then a little water; on standing, the nitrolpiperide crystallised out. It was purified by crystallisation from hot alcohol, from which it separates in the form of small, white, glistening plates. It is but slightly soluble in cold, and not very readily in hot alcohol. When purified by several recrystallisations, it melted at 153°. It was found to contain 8·72 per cent. nitrogen, instead of 8·80 the calculated amount.

It now became necessary to ascertain whether this sesquiterpene was identical with any of the well-known and properly characterised sesquiterpenes obtained from other sources. In the first place, its boiling point, relative density, and optical inactivity, as also its inability to furnish a crystalline dihydrochloride, show that it is not cubebene (cadinene). On obtaining a crystalline nitrosochloride, melting at 164—165°, I was struck by the fact that Wallach (*Annalen*, **271**, 295) had obtained from caryophyllene (the sesquiterpene which occurs in oil of cloves) a nitrosochloride melting at nearly the same temperature, and which appeared from his statements to resemble somewhat closely the one I had obtained. I thought, therefore, that the hop oil sesquiterpene might possibly be inactive caryophyllene. Wallach, in the paper above referred to, has shown that caryophyllene, when boiled in glacial acetic acid solution with dilute sulphuric acid, readily forms a well-crystallised, characteristic alcohol of the formula $C_{15}H_{25}{\cdot}OH$. Attempts to prepare a similar compound from the hop-oil sesquiterpene failed, nothing but dense, oily products being formed, showing not the slightest tendency to crystallise. The conditions prescribed by Wallach were closely followed, a parallel experiment with caryophyllene itself readily yielding the crystalline alcohol. Wallach, moreover, states that the nitrolpiperide obtained from caryophyllene nitrosochloride could not be obtained in the crystalline condition, whereas the corresponding compound from the hop-oil sesquiterpene crystallises readily. There can be no doubt, therefore, that this compound is not caryophyllene. Its relative density and the formation of a nitrosochloride prove that it is not identical with clovene, whilst it differs in several important respects from cedrene.

These are the only sesquiterpenes of which we possess any knowledge sufficiently definite to admit of their identification. The evidence I have given as to its chemical individuality justifies me, I think, in adding to this list the sesquiterpene of the essential oil of hops, for which I venture to propose the name *humulene*.

In three out of the four samples of oil with which I have worked, humulene was, as regards quantity, the main constituent. Since these samples have been prepared in different years from hops grown in several countries under various climatic conditions, the essential oil of hops must be regarded, I think, as one of those oils in which a sesquiterpene figures as an important constituent.

I hope, before long, to be able to render the examination of this essential oil more complete.

IX.—*Solution and Pseudo-Solution. Part II. Some Physical Properties of Arsenious Sulphide and other Solutions.*

By S. E. Linder and Harold Picton.

In Trans., 1892, **61**, 148, will be found an account of the preparation of various "grades" of arsenious sulphide solution. In a subsequent paper, the conclusion is drawn from this and other observations that there is no defined boundary line between suspension, on the one hand, and perfect solution on the other; the difference is only one of degree of aggregation. The previous series of "grades" of arsenious sulphide solution has been added to, and it is now found that the one obtained on pouring a solution containing about 2 per cent. of arsenious oxide, As_4O_6, into sulphuretted hydrogen water is not only diffusible, but can be filtered through a porous pot. The following grades of sulphide solution have now been prepared: As_2S_3 (α), the aggregates of which are visible under the microscope; As_2S_3 (β), invisible, but not diffusible; As_2S_3 (γ) diffusible but not filterable; As_2S_3 (δ), diffusible and filterable, but scattering and polarising a beam of light.

The following experiments have been made on the higher grade solutions, chiefly (γ), the filterable solution (δ) only having been discovered at the close of the experiments described in this section.

Coagulative Power.—Metallic salts are found to arrange themselves in sharply divided groups as regards their power of coagulating these solutions of arsenious sulphide. The group into which a metallic salt will fall depends on the valency of the metal, thus tervalent metals have the highest coagulative power, bivalent metals about one-tenth of this power, and univalent metals (including hydrogen and ammonium) less than one-five-hundredth. These differences are also shown by the same metal when the valency varies (*e.g.*, with iron). It is interesting, however, that silver, and thallium (in thallous salts) should fall in the same group as copper and the bivalent metals, whilst mercury and lead are placed in Group I, along with aluminium, iron, and the tervalent metals.

In the accompanying Table I (p. 65) the comparison is made between molecular weights of the different salts. In this table, the relative quantities needed for coagulation are given, the solutions being of equimolecular strength, and referred to aluminium chloride ($AlCl_3$) as unity. Thus one molecule of aluminium chloride, $AlCl_3$, possesses the same coagulative power as 16·4 mols. of cadmium chloride, or 750 mols. of sulphuric acid (H_2SO_4). The molecular coagulative power of a salt is taken to be inversely proportional to the number of molecules required to produce coagulation. Taking equivalents, the same relationship holds, although the difference between the groups is then, of course, not so striking.

In order to make the comparisons exact, the same arsenic solution was used throughout, and the coagulations were so arranged that the final strengths of the arsenic solutions at the moment of coagulation were identical. To ensure this, the arsenic solution was more or less diluted before commencing the titration, according to indications obtained from preliminary determinations. Slight irregularities might arise from the fact that at the moment of starting the experiment the strengths were not identical; and, moreover, there is another possible source of error, namely, the variation of time employed in the titrations. Unless this is kept approximately the same, serious differences occur, as a quantity of coagulant insufficient to produce coagulation immediately will do so in the course of time. These difficulties were, however, satisfactorily met.

The differences in coagulative power observed between salts of metals of different valency is so very striking, that the coagulative power might afford a convenient test of the valency of a metal in a given compound. We propose to continue our work on the coagulation of low grade solutions.

The true nature of coagulation is at present unknown to us, but some light has been thrown on the subject by a careful examination of the coagulum which separates from a solution of arsenic sulphide, γ, on the addition of a metallic salt. As it was found that barium chloride coagulated the sulphide in a form specially suitable for washing, and as both barium and chlorine can be rapidly and accurately estimated in solution, this salt was selected for experiment. 30 c.c. of a solution of arsenic sulphide, γ (containing about 1 gram of As_2S_3), was diluted to 100 c.c., and coagulated by the careful addition of 10 c.c. of barium chloride solution (containing about 208 grams of the salt to 20 litres), the whole was diluted to 250 c.c. and allowed to deposit the sulphide; 100 c.c. of the clear liquid was then withdrawn, and the barium precipitated as sulphate; the chlorine

TABLE I.—*Coagulative Powers of Metallic Salts.*

Metal.	Chlorides.	Bromides.	Iodides.	Fluorides.	Nitrates.	Sulphates	Oxalates.	Sulphites.	Arsenates.	Phosphates.	Tartrates.
Aluminium....	1·0	—	—	—	—	0·60	—	—	—	—	—
Pot. alum.....	—	—	—	—	—	0·65	—	—	—	—	—
Amm. alum ...	—	—	—	—	—	0·60	—	—	—	—	—
Ferric iron	2·2	—	—	—	—	1·50	—	—	—	—	—
Amm. iron alum	—	—	—	—	—	1·65	—	—	—	—	—
Chromium	—	—	—	—	—	1·25	—	—	—	—	—
Potassium chrome alum	—	—	—	—	—	1·00	—	—	—	—	—
Lanthanum ...	—	—	—	—	—	0·60	—	—	—	—	—
Didymium	—	—	—	—	—	0·65	—	—	—	—	—
Cerium	—	—	—	—	—	0·60	—	—	—	—	—
Lead	3·65	—	—	—	—	—	—	—	—	—	—
Mercury	5·23	—	—	—	—	—	—	—	—	—	—
Cadmium	16·4	15·5	22·7	—	14·6	15·0	—	—	—	—	—
Magnesium....	18·6	21·3	—	—	—	34 1	—	—	—	—	—
Barium	19·1	—	—	—	18·6	—	—	—	—	—	—
Strontium.....	20·0	—	—	—	20·9	—	—	—	—	—	—
Calcium	21·3	21·3	—	—	20·9	26·0	—	—	—	—	—
Zinc	21·8	—	—	—	—	27·3	—	—	—	—	—
Ferrous iron ..	23·1	—	—	—	—	32·7	—	—	—	—	—
Cobalt........	20·9	—	—	—	22·3	31·8	—	—	—	—	—
Nickel........	24·6	—	—	—	—	26·8	—	—	—	—	—
Manganese	—	—	—	—	—	32·8	—	—	—	—	—
Silver	—	—	—	—	20·0	8·8*	—	—	—	—	—
Copper	—	—	—	—	—	14·8	—	—	—	—	—
Thallous	—	—	—	—	—	13·0†	—	—	—	—	—
Hydrogen.....	954	909	933	—	933	750	1,980	3,640	5 110	4,430	—
Ammonium ...	1,010	1,200	1,200	—	1,200	778	818	—	1,140‡	1,460§	—
Potassium.....	1,590	1,640	1,660	1,660	1,700	1,000	795	—	—	—	1,140
Lithium	—	—	—	—	1,770	1,020	—	—	—	—	—
Sodium	1,680	1,770	1,930	1,980	1,800	1,110	—	1,390	—	1,460‖	—

* Ag_2SO_4. † Tl_2SO_4. ‡ $(NH_4)H_2AsO_4$. § $(NH_4)_2HPO_4$. ‖ Na_2HPO_4.

was determined in a second sample. The weights of barium and chlorine found were as follows.

Barium.... 0·02422 Chlorine.... 0·01380

10 c.c. of the same barium chloride solution was diluted to 250 c.c.; 100 c.c. gave

Barium.... 0·02663 Chlorine.... 0·01380

It will be seen that, while the amount of chlorine has remained constant, the barium has sensibly diminished; it has been withdrawn from solution by the sulphide of arsenic, in which it can readily be detected after carefully washing out the excess of barium chloride by cold water; the sulphide is then found to contain very sensible traces of barium, but is free from chlorine.

These experiments when repeated with calcium chloride gave similar results; calcium was withdrawn from solution, whilst the amount of chlorine remained constant. The calcium could be readily detected in the coagulated sulphide even after careful and prolonged washing.

It was found impossible to extract this small trace of barium or calcium by cold water, and even after boiling with water the sulphide was still found to have retained it; similar results were obtained with other metallic salts. If, however, the sulphide, coagulated in this way by the addition of the dilute solution of a metallic salt, be digested for a few minutes with a cold, dilute solution of another salt, a complete exchange is effected between the metals, and the sulphide is found to have entirely lost the small trace of the original metal; the latter can be readily identified in the filtrate, whilst a small quantity of the second metal is found associated with the sulphide, from which it cannot be removed by washing with cold water.

For example, if we coagulate the sulphide with a dilute solution of barium chloride (208 grams to 20 litres), and, after carefully washing to extract all excess of salt, digest the coagulum with dilute calcium nitrate (164 grams to 20 litres), the barium is entirely displaced in the sulphide by calcium, whilst no trace of chlorine can be detected either in the filtrate or in the sulphide. Similarly, the barium can be extracted by potassium nitrate or ammonium chloride; in this case, solutions containing about 1 gram-mol. of salt in 4 litres were employed for extraction. Owing to the difficulty of identifying small traces of potassium and ammonium, and of washing the sulphide free from the excess of the salts employed, it was not found possible to prove the presence of potassium or ammonium in the coagulated sulphide, but there is no reason for regarding the action of these salts as exceptional.

This power which metals possess of displacing one another in their combinations with sulphide of arsenic must be regarded as due to mass-action rather than to selective affinity, although the nature of the metal has considerable influence in determining the stability of the resulting compound, for whilst univalent and bivalent metals in the same salts have widely different powers of coagulating a solution of arsenious sulphide, it is yet possible to completely displace a bivalent metal like calcium by simple digestion with a solution of an ammonium or potassium salt of appropriate strength; moreover, two metals can displace one another in the same simple way. Thus, cobalt can easily be made to displace calcium in the sulphide of arsenic coagulated by calcium chloride by extracting the precipitated sulphide, after careful washing, with a solution of cobalt chloride, or sulphate, whilst, in the same way, using cobalt salts to coagulate the sulphide, the cobalt, which is invariably found associated with the sulphide, can be readily displaced by calcium.

An additional point of interest is that when salts of the same group are added successively to produce coagulation, the effect is additive, but with salts of different groups this is not the case. Thus to coagulate 26 c.c. of the arsenious sulphide solution, there were needed either 4·9 c.c. of ammonium chloride solution (26·7 grams per litre) or 4·20 c.c. of hydrochloric acid (18·3 grams HCl per litre), but on first adding 2·00 c.c. of the ammonium chloride solution, only 2·4 c.c. of hydrochloric acid were needed to complete coagulation, the calculated amount being 2·5 c.c.

TABLE II.—*Coagulation by Successive Additions of different Salts of the same Group.*

Salt A.	Volume A.	Salt B.	Volume B required to complete coagulation.	Calculated volume of B required.
		Hydrochloric acid ..	4·20	
Ammonic chloride....	4·90			
Ammonic chloride....	2·00	Hydrochloric acid ..	2·40	2·50
Hydrochloric acid....	2·60	Ammonic chloride..	1·75	1·85
		Nitric acid.........	4·10	
Hydrochloric........	2·35	Nitric acid.........	1·97	1·80
		Potassium sulphate.	4·40	
Nitric acid	2·00	Potassium sulphate.	1·95	2·25
Ammonic chloride....	2·00	Potassium sulphate.	2·40	2·60
Calcic Nitrate	4·60			
		Baric chloride......	4·20	
Calcic Nitrate	2·20	Baric chloride......	2·30	2·20

TABLE III.—*Coagulation by Successive Additions of Different Salts of Different Groups.*

Volume of salt A (potassium chloride).	Volume of salt B (strontium chloride) required to complete coagulation.	Calculated volume of B necessary.	Difference.	Volume of salt A (strontium chloride)	Volume of salt B (hydrogen chloride) necessary to complete coagulation.	Calculated volume of B necessary.	Difference.
0·00	4·40			0·00	4·15		
0·30	4·90	4·20	+0·70	0·30	4·10	3·87	+0·23
0·60	5·40	4·00	1·40	0·60	4·15	3·59	0·56
0·90	5·50	3·80	1·70	0·90	4·00	3·31	0·69
1·20	5·55	3·60	1·95	1·20	3·87	3·03	0·84
1·50	5·70	3·40	2·30	1·50	3·70	2·75	0·95
1·80	5·90	3·20	2·70	1·80	3·60	2·47	1·13
2·10	6·00	3·00	3·00	2·10	3·45	2·19	1·26
2·40	5·70	2·80	2·90	2·40	3·38	1·91	1·47
2·70	5·65	2·60	3·05	2·70	3·05	1·63	1·42
3·00	5·30	2·40	2·90	3·00	2·75	1·35	1·40
3·30	5·10	2·20	2·90	3·30	2·35	1·07	1·28

With potassium chloride and strontium chloride, on the other hand, the effect is not additive. Indeed, strange as it may seem, the amount of strontium chloride needed for coagulation is actually increased by the previous addition of potassium chloride. We also observe that up to a certain point the more potassium chloride is added the more strontium chloride is needed to produce coagulation; but when the proportion of potassium chloride exceeds this limit, any further addition of that salt begins to diminish the amount of strontium chloride needed to induce coagulation. The results were carried as far as they could be short of complete coagulation by potassium chloride.

The reverse titration was tried with strontium chloride and hydrogen chloride. It also shows a maximum inhibitory effect by the strontium chloride.

Coagulative Power and Dissociation.—As it appears probable that the power metallic salts have of coagulating arsenious sulphide is entirely due to the positive radicle, it is of interest to inquire whether the coagulative power of salts of the same metal is proportional to the number of free positive ions in the solution from which the sulphide of arsenic separates.* That some close connection exists between dissociation and coagulative power is at once evident from an examination of the table of relative coagulative powers of metallic salts (Table I, p. 65). It will there be seen that hydrogen in the acids which readily dissociate in solution, such as hydrochloric, hydrobromic, hydriodic, nitric, and sulphuric acids, has a considerably greater coagulative power than it has in less dissociated acids, such as oxalic, phosphoric, and arsenic acids, whilst it has been found impossible to coagulate arsenious sulphide solution at all by means of tartaric, succinic, or acetic acids, which are practically non-dissociated.

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* In the case of univalent metals, this contains about 1 mol. weight of the salt

In comparing the coagulative powers of salts of the same group, we must make the comparison between equivalent rather than between molecular weights of the salts. If we make the assumption that the "equivalent" coagulative power, c, of a salt is proportional to the number of free positive ions in the solution from which the sulphide of arsenic separates, and to some constant θ dependent on the nature of the positive radicle in the salt employed, we have

$$\frac{c}{c'} = \frac{x\theta}{x'\theta'}$$

where c and c' are the equivalent coagulative powers of two salts, θ and θ' constants depending on the metals, and x and x' proportional to the number of salt molecules dissociated into free ions (the values of x and x' are calculated from the electrical conductivities). For salts of the same metal, $\theta = \theta'$, and the equation reduces to

$$c/c' = x/x'.$$

The truth of this equation is proved by the results given in the following table, in which the equivalent coagulative powers and the dissociations are compared for the chlorides, nitrates, and sulphates of hydrogen and potassium both referred to the chloride as unity.

TABLE IV.

Acid.	Hydrogen.		Potassium.	
	Coagulative power.	Dissociation.	Coagulative power.	Dissociation.
Cl	1·00	1·00	1·00	1·00
NO_3	1·02	1·00	0·93	0·99
$SO_4/2$....................	0·64	0·66	0·80	0·82

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in 10 litres; in that of bivalent metals about 1 mol. weight in 500 litres; whilst in the case of the tervalent metals the sulphide is found to separate from a solution containing 1 mol. weight of the salt in 10,000 litres.

Now, the molecular conductivity of a salt has been shown by Kohlrausch to be of the form

$$\mu = x(u + v)$$

where μ is the molecular conductivity, x the proportion of the electrolyte dissociated into its ions, and u and v the velocities of migration of the ions.

We have, therefore, for the molecular conductivity of two salts

$$\frac{\mu}{\mu'} = \frac{x\,(u + v)}{x'\,(u' + v')}.$$

If salts of the same metal be compared, $u = u'$, and, further, v has a value not far removed from v' for the chlorides, iodides, bromides, nitrates, and sulphates. The equation will therefore approximately take the form $\mu/\mu' = x/x'$, and we should expect to find that the equivalent coagulative powers of two salts of the same metal are proportional to the equivalent conductivities of the salts for the same strength of solution as that from which the sulphide coagulates. Thus

$$\frac{\mu}{\mu'} = \frac{x}{x'} = \frac{c}{c'}.$$

In the following table, V, are tabulated the equivalent conductivities and the equivalent coagulative powers for the chlorides, bromides, iodides, nitrates, and sulphates of potassium, hydrogen, sodium, and ammonium, in each case referred to the nitrate as unity: the agreement between the two sets of figures is close.

TABLE V.—*Relative Equivalent Conductivities and Coagulative Powers compared.*

	Potassium.		Hydrogen.		Sodium.		Ammonium.	
Acid.	Molecular conductivity.	Coagulative power.	Molecular conductivity.	Coagulative power.	Molecular conductivity.	Coagulative power.	Molecular conductivity.	Coagulative power.
Cl ..	1·07	1·07	0·94	0·98	1·05	1·07	1·02	1·19
Br ..	1·08	1·04	0·99	1·03	1·06	1·05	1·10	1·00
I....	1·08	1·04	1·01	1·00	1·05	0·93	1·09	1·00
NO_3	1·00	1·00	1·00	1·00	1·00	1·00	1·00	1·00
$SO_4/2$	0·85	0·85	0·62	0·62	0·83	0·81	0·82	0·77

From the above experiments it would seem, therefore, that the coagulative power is entirely controlled by the number of free positive ions present in the sulphide solution at the moment of coagulation, and, further, that some action takes place between the sulphide of arsenic and the metallic salt; the nature of this action, however, is very doubtful, and no satisfactory explanation can be offered.

Specific Gravity.—The relation between specific gravity and dilution of arsenious sulphide solutions is represented by a straight line.

The following table gives the specific gravities of arsenious sulphide solutions of varying strength. In the case of solutions of metallic salts, *e.g.*, potassium chloride of ordinary strength (down to 1 per cent.), the relation between specific gravity and dilution is not a straight line. The same holds for strong solutions of cane sugar, which, however, below a strength of about 7 per cent., behaves like arsenious sulphide.

TABLE VI.—*Specific Gravities of Arsenious Sulphide Solutions.*

Solution employed.	Strength of solution.	Specific gravity found at 22°.	Specific gravity calculated, assuming that the relation between specific gravity and percentage strength is represented by a straight line.	Difference.
Arsenious sulphide (γ)	4·4* per cent.	1·033810		
,, ,,	2·2 ,,	1·016880	1·016905	−0·000025
,, ,,	1·1 ,,	1·008435	1·008440	−0·000005
,, ,,	0·55 ,,	1·004200	1·004218	−0·000018
,, ,,	0·275 ,,	1·002110	1·002100	+0·000010
,, ,,	0·1375 ,,	1·001050	1·001055	−0·000005
,, ,,	0·06875 ,,	1·000535	1·000525	+0·000010
,, ,,	0·03438 ,,	1·000267	1·000267	0·000000
,, ,,	0·01719 ,,	1·000137	1·000134	+0·000003

* This was the strongest solution obtainable.

Volume-change.—As confirming the above, it is interesting to note that there is absolutely no volume-change on coagulation of a solution. The method adopted was as follows. A large bottle, capacity 750 c.c., was fitted with a ground glass stopper carrying a capillary tube. The capacity of 10 mm. of this tube was 0·0133 c.c. The arsenious sulphide solution was coagulated by adding calcium chloride contained in a glass bulb with a very fine stem. As the calcium chloride itself produced contraction on mixing with water, the amount of this was first determined with a known weight of calcium chloride, and the same weight was used in the coagulation experiment. The instrument was, of course, exceedingly sensitive to temperature changes, responding to a change of 0·05°. On this account, the flask was kept immersed in a current of water of uniform temperature. After coagulation, the readings were continued till the level was absolutely constant. The results show that the volume-change noticed on coagulation is precisely that due to the calcium chloride and water.

TABLE VII.—*Volume-change on Coagulation of Arsenious Sulphide*

Liquid in bottle.	Calcium chloride used for coagulation.	Fall of liquid in capillary tube.	Volume alteration.
Distilled water..........	1·7870 grams.	13·3 mm.	0·0177 c.c.
" "	1·7870 "	13·0 "	0·0174 "
Arsenious sulphide (γ) .. (1·25 per cent. solution.)	1·7870 "	13·1 "	0·0175 "

Surface-Tension.—So far as could be ascertained with the instrument employed, the surface-tension of water is unaffected by the dissolved arsenious sulphide. The instrument used consisted of a capillary tube graduated in millimeters, and, to avoid the effect of inequalities in the bore, the tube was so arranged that the liquid always stood at the same division. In carrying out the experiments, the tube was washed first of all very carefully with soda and hot aqua regia, and finally with water. The liquid examined was next drawn through the tube for some time, and then allowed to sink until the level became stationary; the liquid was next forced below this level and allowed to rise. If the two readings coincided, the result was considered satisfactory. In the comparative experiments the temperature was kept within variations of at most 0·05°.

A 2 per cent. solution of arsenious sulphide gave a capillary rise of 387·5 mm., the calculated rise being 387·7 mm., a difference of — 0·2 mm. On the other hand, a 2·5 per cent. solution of cane sugar gave a rise of 384·7, the calculated rise being 383·8, a difference of + 0·9 mm. This difference, though not large, is quite appreciable, and with stronger sugar solutions the differences increase in the same direction. With the sulphide, on the other hand, the rise is at one time 0·2 mm. too low; at another 0·1 mm. too high.

Osmotic Pressure.—Notwithstanding a large amount of work on this subject, we have been unable to obtain satisfactory results.

Quantitative comparisons seem at present impossible, the pressure being variable with different pots, and also from causes that escape detection. Using an apparatus such as that described by Adie (Trans., 1891, **59**, 344), but with the porous pot and gauge filled with water, the gauge open to the air, and with arsenious sulphide solution outside the pot, a 4 per cent. solution was found with one pot to give 17 mm. water pressure. Hæmoglobin in solution also gave a small pressure, as did also Rowney's water-colour indigo. A coarse indigo suspension composed of particles visible with a 1-inch objective, gave no pressure. Filterable substances were found to give no permanent pressure. We merely mention these results as preliminary, and hope in time to obtain more evidence.

New Solutions.—Among new solutions examined may be mentioned, in addition to As_2S_3 (δ), Chapman's uranium and ferric dextrosates. Both of these, when pure, scatter light, and are non-filterable. The latter, however, in presence of ammonia and ammonium chloride, does not scatter light, and is filterable. Two complicated tungstates, described by Wolcott Gibbs (*Proc. Amer. Acad.*, **15**, 1; **16**, 126; **18**, 271, &c.), have also been examined. The barium salt, $20WO_3,P_2O_5,6BaO + 48H_2O$, showed no luminous beam, and was readily filterable. So, too, with the more complex salt $60WO_3,3P_2O_5,V_2O_5,VO_2,18BaO + 150H_2O$; Gibbs regards this salt as a chemical unit, since it exhibits the same composition when prepared under varying conditions.

Degradation of As_2S_3 (δ).—As regards the filterable As_2S_3 (δ), the following points may be recorded. On adding a few drops of very dilute sodium chloride to this solution, it became at once non-filterable, and, therefore, degraded in the scale of solution. This result is interesting as suggesting that a coagulant acts by increasing the size of *all* the aggregates present in a solution, and probably to a similar extent. The pot used in this case was found, after careful extraction, to completely prevent the filtration of ferric hydrate, even after addition of ferric chloride. Strong arsenious sulphide solutions (4 per cent.) seem also to be uniformly non-filterable.

Filtration of Dyes.—Methyl-violet, Hofmann's violet, and magenta, though not scattering light, were found to be non-filterable. This apparently anomalous result was explained when it was found that on exposing solutions of the dyes to the action of fragments of pot they were withdrawn from solution; in this case we have a special selective action of the material quite different from the true filtration of arsenious sulphide, &c., which are not withdrawn from solution.

Effect of Low Temperature and Keeping.—On freezing a solution of arsenious sulphide (γ) the whole of the sulphide comes out of solution, but if alcohol be added to prevent freezing and the temperature is then lowered with ice and salt, no coagulation occurs. The same observations have been made with ferric hydrate solution. A solution of arsenious sulphide of about 2 per cent. strength, prepared three years ago (August 17th, 1891), shows as yet no signs of coagulation.

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X.—*Contributions to the Chemistry of Cellulose. I. Cellulose-sulphuric acid, and the Products of its Hydrolysis.*

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IN 1819, Braconnot (*Ann. Chim. Phys.*, 1819, [2], 12, 185) observed that linen dissolved in concentrated sulphuric acid, and that if the liquid was diluted with water, a clear solution was obtained, containing, besides sulphuric acid, another acid which he named *acide végéto-sulphurique*. When the diluted solution was boiled for some hours, a substance was produced which was fermentable, and which he consequently considered to be glucose.

In 1844, Blondeau de Carolles (*Ann.*, 1844, 52, 412) investigated this acid, and found that when cotton-wool was added to concentrated sulphuric acid, it dissolved and formed a light yellow solution, which changed to dark violet on standing. When the solution was diluted with cold water and neutralised with barium carbonate, the excess of sulphuric acid was precipitated as barium sulphate, and the barium salt of cellulose-sulphuric acid remained in solution; this was precipitated from the concentrated clear solution, on adding strong alcohol. The composition of these salts varied with the time the sulphuric acid solution of cellulose was allowed to stand before diluting.

$C_{18}H_{36}O_{18}(SO_3)_2BaO,2H_2O$ was obtained after ½ hour.
$C_{10}H_{20}O_{10}(SO_3)_2BaO,2H_2O$ „ „ 12 hours.
$C_4H_8O_4(SO_3)_2BaO,2H_2O$ „ „ 24 „

About the same time, H. Fehling (*Ann.*, 1845, 53, 135) found the composition of one of the barium salts to be BaO, 5 per cent.; SO_3, 5·3 per cent.; C. 35·8 per cent.; H, 5·9 per cent., which corresponds to $C_{90}H_{180}O_{90}BaO(SO_3)_2$. Marchand (*J. pr. Chem.*, 1845, 35, 200) acted on Swedish filter paper with sulphuric acid for four weeks, and obtained a lime salt, $C_{23}H_{28}O_8(SO_3)_2CaO$.

Béchamp (*Ann.*, 1856, 100, 364) added little to the knowledge of these acids. He states that the substance obtained by dissolving cellulose in sulphuric acid is a dextrin, like starch dextrin, but with less specific rotatory power, and that on boiling this with acids a sugar is formed.

In 1883, Flechsig (*Zeit. physiol. Chem.*, 1883. 7, 523) determined the nature of the sugar formed when cellulose-sulphuric acid is hydrolysed. He used cotton-wool cellulose, diluted the solution of cellulose in sulphuric acid until it contained 2 per cent. sulphuric acid, and boiled this for 5—6 hours. The solution, neutralised with baryta, filtered, and concentrated, yielded crystals of sugar which were recrystallised. Only about 3 per cent. sugar appears to have been obtained. The specific rotatory power was found to be $[\alpha]_D = + 53·0$, which is practically that of dextrose. The cupric reducing power is identical with that given by Allihn (*J. pr. Chem.*, **130**, 61) for dextrose, but these numbers are about 10 per cent. higher than those usually accepted for dextrose. Flechsig found that 1 gram of the sugar reduced 1·940 grams of copper. The usual figures are 1 gram dextrose reduces 1·760 grams of copper.

Lindsey and Tollens (*Ann.*, 1891, **267**, 370) dissolved cellulose, obtained from wood by the sulphite process, in strong sulphuric acid, and boiled the diluted solution for some hours. They separated from this about 3½ per cent. of crystalline sugar $[\alpha]_D = + 52·7$, which appears to be dextrose.

In 1885, Hönig and Schubert (*Monatsh.*, 1885, **6**, 708) investigated these substances, employing cotton-wool cellulose. They confirmed the fact observed by Blondeau de Carolles, that the proportion of barium to sulphuric acid is invariably one equivalent of the former to two of the latter.

The temperature at which the cellulose was dissolved in sulphuric acid was found to have very little effect on the composition of the compounds, but a considerable effect on the optical activity, the latter varying directly with the temperature. The following table illustrates this.

Temp.	Per cent. Ba.	$[\alpha]_D$.
7°	25·4	− 3·7
10	26·7	− 1·6
20	26·8	+37·1
25	24·3	+44·1
30	26·9	+59·5
33	25·4	+57·4
40	25·3	+73·0

The proportion of acid to cellulose did not affect the composition or optical activity, so long as it did not fall below two of acid to one of cellulose; if the proportion was reduced to one of acid to one of cellulose, the resultant cellulose-sulphuric acid neutralised less base.

The time during which the sulphuric acid solution was kept before dilution had only a slight influence on the composition, and rather more effect on the optical activity of the compounds; if it was short, the amount of base neutralised and optical activity were low. Thus a solution which stood only ½ hour before diluting gave a barium salt containing 24·3 per cent. Ba and $[\alpha]_j = 44·1$; whereas the same solution, on standing 24 hours before dilution, gave a barium salt containing 25·7 per cent. Ba and $[\alpha]_j = 67·8$. Some of the barium salts were fractionally precipitated from their aqueous solutions by alcohol, but in nearly every case the fractions were found to be identical.

The barium salts of these acids were white or yellow powders, which appeared to be crystalline, easily soluble in all proportions in water but insoluble in alcohol. They were optically active, and reduced Fehling's solution, reducing it less if they had been prepared at a low temperature than when prepared at a high temperature. When boiled in aqueous solution, the barium salts were decomposed, the products being barium sulphate and an organic barium salt containing less barium than the original salt, but no sugar. These experiments were, however, few in number; no attempt was made to purify the barium salt, and the proof of the absence of sugar appears to be very incomplete.

They give $C_{6n}H_{10(n-x)}O_{5(n-x)}(SO_4M')_x$, as the general formula of these products, but, as no determination of carbon or hydrogen was made, it is difficult to see what evidence there is for this.

From a solution of cellulose in sulphuric acid diluted with 15—20 times its weight of absolute alcohol, and allowed to interact during several days, a product separated, which was collected, and washed with alcohol until the filtrate was no longer acid; this substance yielded a barium salt containing 4—6 per cent. barium. When the alcoholic compound was boiled with excess of alcohol, it was decomposed, producing ethyl hydrogen sulphate, and a substance having a composition corresponding with $C_6H_{10}O_5$, and which was optically active, $[\alpha]_j = +89·3$.

In a later paper (*Monatsh.*, 1886, 7, 455), Hönig and Schubert gave an account of further work on this subject. The dextrin reduced Fehling's solution, but did not contain sugar; it had no action on Barfoed's solution (a solution of copper acetate in dilute acetic acid). This is, however, not altogether satisfactory, as, although dextrose acts on this, there are many sugars that do not. It is evident this compound is not the same as starch dextrin.

The problem of the constitution of cellulose is as yet far from solved. Almost the sole facts of which there is any definite proof are that its empirical formula is $C_6H_{10}O_5$, and that it contains some hydroxyl groups, the evidence as to their number being somewhat conflicting.

It appeared probable that the study of the cellulose-sulphuric acids and the products of their hydrolysis would lead to the acquirement of some knowledge of the constitution of cellulose. These compounds are hydrolysed by boiling with dilute sulphuric acid, it is stated with the production of dextrin and sugar. The only facts there are to bear out this is that a small percentage of sugar has been obtained from amongst the transformation products.

Purified cotton-wool, as sold for medical purposes, was considered to be practically pure cellulose. It was but very slightly acted on when treated first with bromine water, and then with weak ammonia. It was employed throughout these experiments.

The cellulose-sulphuric acids were prepared in the following manner. A weighed quantity of sulphuric acid (the pure acid of commerce) was cooled to the required temperature. Dried cotton cellulose was added gradually, until the acid would dissolve no more, care being taken that the temperature did not appreciably rise; this operation usually took about three hours. The solution, after having stood about four hours longer at the same temperature, was diluted with cold water, and neutralised with baryta. The barium sulphate was allowed to settle, the clear solution poured off, and the precipitate washed by decantation; the solutions were then concentrated, first on a water bath, and finally to a syrup in a vacuum. It was proved that, if care were taken, the solution remained neutral, and that no alteration in composition took place during evaporation. The barium salt, which was obtained as a syrupy precipitate on adding alcohol to the concentrated solution, was purified from compounds soluble in alcohol, such as sugar, by repeatedly dissolving in water and precipitating with alcohol. The syrupy precipitate was dried by first treating it with absolute alcohol, when it became brittle and powdery, then exposing it in a vacuum over strong sulphuric acid, and finally heating in dry air at 100° for 6—12 hours.

The barium salts thus prepared are white or slightly coloured, hygroscopic, amorphous powders, very soluble in water, but insoluble in alcohol and ether. They are not altered when heated at 100°, but at a slightly higher temperature they are blackened, and when strongly heated are decomposed with almost explosive violence.

The free acids are obtained in aqueous solution by adding sulphuric acid to a solution of the barium salt as long as a precipitate is formed. Their aqueous solutions are decomposed when heated, and they are soluble in alcohol.

As the barium salts are so much more convenient to manipulate than the free acids, they have been employed throughout this work. In order to determine if they were pure, they were fractionally precipitated by alcohol. The most insoluble fraction is always designated by the lowest number: thus Fraction 1 is more insoluble than Fraction 2, and so on.

In all cases, the percentage of barium, the optical activity, and the cupric reducing power were determined; also, in most cases, the percentage of sulphuric acid. These factors were determined as follows:—The dry substance was dissolved in water, and the solution made up to a definite bulk. The optical activity was measured by a Laurent polariscope, which gave α_D. The barium was determined by precipitating a measured quantity of the solution with sulphuric acid. The cupric reducing power, K, by boiling another portion of the solution for 10 minutes with Fehling's solution diluted with an equal volume of water. The K was calculated in the usual way; compared with dextrose, K = 100. (0·4535 gram dextrose yields 1 gram CuO.) As Fehling's solution contains a sulphate, it might be expected to precipitate the barium which is present; however, if there is an excess of Fehling's solution this does not take place. The copper oxide must always be tested for barium, and if any is present it must be estimated and allowed for. The sulphuric acid was estimated by boiling a portion of the solution for some hours with strong hydrochloric acid and a little barium chloride. It was found by experiment that if sufficient hydrochloric acid was used, and the boiling continued long enough, the whole of the sulphuric acid was precipitated as barium sulphate. Thus, in one case, oxidation with nitric acid yielded 24·0 per cent. SO_4, and boiling with hydrochloric acid 23·9 per cent. SO_4.

In most cases, however, it was found to be more expeditious not to dry the whole of the barium salt, but to dissolve the approximately dry substance in water, and estimate the amount of dry matter by evaporating a measured quantity to dryness in a flat-bottomed platinum dish on the water bath, and heating at 100° in a current of dry air until constant. The barium could then be estimated in this by burning, and converting the ash into sulphate by moistening with sulphuric acid and re-igniting.

The decomposition of the barium salts which contain a high percentage of sulphuric acid is started by the slightest trace of acid, so that it is necessary, when analysing these by the above method, to render the solution slightly alkaline before evaporation by adding a few drops of dilute baryta water. The amount of barium thus added is allowed for when calculating the results.

When it was possible to dry a sufficient quantity of pure salt, determinations of carbon and hydrogen were made by burning in a closed tube with lead chromate.

Composition of the Product formed on dissolving Cellulose in Sulphuric acid.

a. Cellulose dissolved at 5°.—From 20 grams cellulose, Fractions 1, 2, 3, and 4 were prepared. Fractions 1 and 4 were small, amounting to about 1 gram each. Fractions 2 and 3 were the chief portions, and weighed about 7 grams each; they were analysed, with the following results.

	Calculated for $C_6H_8O_3(SO_4)_2Ba$.	Found.	
		Fraction 2.	Fraction 3.
Ba	30·0	31·4	32·0
SO_4........	42·0	44·0	44·1
$[\alpha]_D$ for barium salt =		+ 22°	+ 26°
K =		0	0

The slightly high numbers are accounted for by the occurrence of a small amount of decomposition on drying.

Fraction 4 was also analysed: it gave practically the same numbers.

b. Cellulose dissolved at 15°.—From 28 grams cellulose, Fractions 1, 2, and 3 were prepared. Fractions 1 and 2 amounted to 10 grams each, Fraction 3 about 1 gram; 1 and 2 were analysed.

	Theory for $C_6H_8O_3(SO_4)_2Ba$.	Found.	
		Fraction 1.	Fraction 2.
Ba	30·0	29·9	29·7
SO_4........	42·0	41·7	40·9
$[\alpha]_D$ for barium salt =		+ 56°	+ 53°
K =		0	0

It is therefore evident that the same substance is produced on dissolving cellulose in sulphuric acid at different temperatures; but that its optical activity is dependent on the temperature of dissolution. This confirms Hönig and Schubert's work, but they did not succeed in preparing cellulose-disulphuric acid. They found a percentage of barium of from 24·3 to 26·8. From experiments to be described below, it appears probable that they were dealing with a decomposition product.

Yield of Cellulose-sulphuric acid.

In these two sets of experiments, the yield of cellulose-sulphuric acid was very small; in the first, 20 grams of cellulose gave 16 grams of barium salt, which are equivalent to 5¾ grams of cellulose; in the second, 28 grams of cellulose gave 21 grams of barium salt, which are equivalent to 7½ grams of cellulose. That is, the yield is only about 25 per cent. of the theoretical. To clear up this, a careful experiment was made as follows. 17½ grams of pure, dry cotton cellulose was dissolved in 120 grams of sulphuric acid at 3—5°. After dilution and neutralisation, the soluble matter was separated from the barium sulphate as far as possible by decantation. In this way, there were obtained 2200 c.c., sp. gr. 1·00585, and containing 0·860 gram of dry substance per 100 c.c. This was analysed, and gave the following numbers.

	Theory for $C_6H_8O_3(SO_4)_2Ba$.	Found.
Ba	30·0	30·3
SO_4..............	42·0	43·5

Weight of barium cellulose-sulphate 19 grams, with the partially washed barium sulphate there remained about 4 grams. So that 17·7 grams of cellulose gave 23 grams of barium cellulose-sulphate, equivalent to 8·3 grams of cellulose. That is 48 per cent. of the theoretical yield.

The remainder of the organic matter must remain in an insoluble form, in some way combined with the very large quantity of barium sulphate (about 300 grams). It was only possible to estimate approximately whether this was so, and the experiment indicated 9 grams of organic matter, but it was not found possible to separate it.

Are the Products obtained by dissolving Cellulose in Sulphuric acid at different Temperatures chemically or only physically different?

The products of their hydrolysis by dilute sulphuric acid may throw some light on this. The two barium salts described above and prepared at 5° and 15° respectively, were dissolved in water, and after sufficient sulphuric acid had been added to give a solution containing 2 per cent. of free sulphuric acid, they were heated at 100° for 30 minutes. The neutralised concentrated solutions were fractionated by precipitation with alcohol with the following results.

a. Hydrolysis of Cellulose-disulphuric acid prepared at 5°.—10 grams of the original barium salt gave 2 grams of Fraction 1, 1¼ grams of Fraction 2, ½ gram of Fraction 3. Fraction 1 was purified by repeatedly dissolving in water and precipitating by alcohol, Fraction 2 was precipitated by adding strong alcohol (0·820) to the concentrated alcoholic solution, and Fraction 3 remained in solution; it would, therefore, contain the sugars, if any.

	Theory for	Found.	
	$C_{18}H_{28}O_{13}(SO_4)_2Ba$.	Fraction 1.	Fraction 3.
Ba	17·5	17·7	9·0
SO_4........	24·6	24·2	—
$[\alpha]_D$ for barium salt =		+ 25°	+ 26°
K =		23·3	71·3

Fraction 2 was also analysed; it gave the percentage of Ba and SO a little lower than Fraction 1, and K and $[\alpha]_D$ higher, but as it could not be considered to be properly purified, the numbers are of little consequence.

The high K of Fraction 3 indicates that sugar is probably present. A portion of the solution containing 0·34 gram of substance was digested for 30 minutes with 1 gram of phenylhydrazine hydrochloride and 1½ grams of sodium acetate; a yellow, crystalline osazone separated, which, when dried, weighed 0·2 gram. Under these conditions, I have always found dextrose, galactose, and invert sugar to give rather more than their own weight of osazone. When recrystallised from alcohol, it melted at 188°, whilst a comparative experiment made with dextrosazone, showed a melting point of 202°. From the percentage of barium, K, and yield of osazone, Fraction 3 appears to consist of a mixture of about half Fraction 1 and half sugar.

The chief product of this transformation is evidently the cellulose-sulphuric acid, $C_{18}H_{28}O_{13}(SO_4H)_2$; 3½ grams of barium salt were obtained, which are equivalent to 9½ grams of the original barium salt, $C_6H_8O_3(SO_4)_2Ba$. 10 grams of barium salt were originally taken—the remaining ½ gram is accounted for by the sugar found.

The reaction may be expressed by the following equation.

$$3.C_6H_8O_3(SO_4H)_2 + 4.H_2O = C_{18}H_{28}O_{13}(SO_4H)_2 + 4.H_2SO_4.$$

b. Hydrolysis of Cellulose-disulphuric acid prepared at 15°.—17 grams of the original barium salt gave 2 grams of Fraction 1, 1½ grams of Fraction 2, 0·5 gram of Fraction 3, and 1¾ grams of Fraction 4; the latter remained in the alcoholic solution, and will therefore contain the sugars, if any.

	Theory for $C_{18}H_{28}O_{13}(SO_4)_2Ba$.	Found.	
		Fraction 1.	Fraction 4.
Ba	17·5	17·6	4·6
SO_4	24·6	24·4	—
$[\alpha]_D$ for barium salt =		+ 75°	+ 54°
K =		18·1	73·7

Fraction 2 gave similar numbers, the percentage of Ba and SO_4 being slightly lower and the K higher.

About 1 gram of Fraction 4 was heated at 100° with 2 grams of phenylhydrazine hydrochloride and 3 grams of sodium acetate for one hour; the yellow, crystalline osazone which separated weighed 0·6 gram when dried. After recrystallisation from alcohol, it melted at 189°, dextrosazone melting at the same time at 202°; these numbers seem to indicate that about one-half of Fraction 4 consists of Fraction 1, and the other half of sugar.

In this transformation, the chief product, as in the previous one, is the cellulose-sulphuric acid, $C_{18}H_{28}O_{13}(SO_4H)_2$; 5 grams of its barium salt were obtained, which are equivalent to 13½ grams of the original barium salt $C_6H_8O_3(SO_4)_2Ba$. The sugar obtained (1 gram) accounts for 2½ grams of the original barium salt, accounting altogether for 16 grams as against 17 grams taken.

It is thus proved that the same cellulose-sulphuric acid is formed in both these experiments. The optical activities still differ in the same way as before hydrolysis; and it will be seen throughout this paper that the cellulose-sulphuric acids, whether the original acids formed by the dissolution of cellulose, or the products of their hydrolysis, always have an optical activity dependent on the temperature at which the original cellulose-disulphuric acid was formed.

In researches on the gum acids, O'Sullivan (Trans., 1884, **45**, 41, and 1891, **59**, 1029) showed that there are two well-marked stages in the hydrolysis; in the first, the gum acids are quickly hydrolysed to gum acids of lower molecular weight, and arabinose; in the second, the hydrolysis proceeds much more slowly, gum acids of still lower molecular weight, and galactose being formed. Preliminary experiments with cellulose-disulphuric acid indicated that the hydrolysis of this also, took place in two stages; in the first, sulphuric acid was separated, but no sugar; in the second, more sulphuric acid was separated, and also sugar. The following transformations were made to determine if these two stages did exist, and, if so, to mark their limits.

Hydrolysis of Cellulose-disulphuric acid.—Stage I.

In all cases, except when otherwise stated, the hydrolysis was effected in solution containing 2 per cent. H_2SO_4 at 100°.

a. Seven Minutes' Hydrolysis of Cellulose-disulphuric acid prepared at 15°.—From 17 grams of cellulose, there were obtained 9 grams of Fraction 1, 7 grams of Fraction 2, 1½ grams of Fraction 3, and 0·3 gram of Fraction 4, which remained in the alcoholic solution; these were analysed with the following results.

	Calculated for $[C_6H_8O_3(SO_4)_2Ba]_2$ $(C_6H_9O_4\,SO_4)_2Ba$.	Found.				
		Fraction 1.			Fraction 2.	Fraction 3.
C......	18·8	—	17·5	17·4	—	—
H	2·2	—	2·34	2·39	—	—
Ba.....	26·8	26·1	—	—	26·3	25·8
SO_4....	37·6	36·7	—	—	36·9	36·5
$[\alpha]_D$ for barium salt =		+ 53°	—	—	+ 52°	+ 51°
K =		0	—	—	0	—

Fraction 4 will contain the sugar, if any; there was only 0·3 gram of it—insufficient to make any accurate analysis. It contained barium, and reduced Fehling's solution. K = 20 approximately. Heated with phenylhydrazine hydrochloride and sodium acetate, it gave only a tarry precipitate, nothing of the nature of an osazone. It is, therefore, proved that no sugar is formed down to this stage of the hydrolysis.

The reaction may be represented by the following equation.

$$2C_6H_8O_3(SO_4H)_2 + H_2O = C_6H_8O_3(SO_4H)_2{\cdot}C_6H_9O_4(SO_4H) + H_2SO_4.$$

b. Fifteen Minutes' Hydrolysis of Cellulose-disulphuric acid prepared at 15°.—Fractions 1, 2, 3, 4 and 5 were prepared. Fractions 1 and 2 formed the bulk of the product, and Fraction 5 remained in solution in alcohol.

	Calculated for $(C_6H_9O_4SO_4)_2Ba$.	Found.		
		Fraction 1.	Fraction 2.	Fraction 4.
Ba	22·1	24·2	23·4	22·6
SO_4........	31·2	31·7	31·6	30·9
$[\alpha]_D$ for barium salt =		+ 51°	+ 48°	+ 38°
K =		0	0	small

Fraction 3 was not analysed, as the figures obtained for Fraction 4 showed that the latter was practically the same as Fractions 1 and 2.

Fraction 5 was fractionally precipitated by ether. The ether precipitate gave K = 20·2. It contained barium and sulphuric acid. The substance remaining in the ether alcohol solution was very small in quantity. It was optically inactive, and reduced Fehling's solution to about the same extent as Fraction 5. When heated with phenylhydrazine hydrochloride and sodium acetate, it yielded no osazone. It is evident that no sugar is formed down to this stage of the hydrolysis.

The reaction may be expressed by the following equation.

$$C_6H_8O_3(SO_4H)_2 + H_2O = C_6H_9O_4{\cdot}SO_4H + H_2SO_4.$$

c. Twenty Minutes' Hydrolysis of Cellulose-disulphuric acid prepared at 5—7°.—Thirty grams of cellulose gave 17 grams of Fraction 1, 2½ grams of Fraction 2, 2 grams of Fraction 3, and 2 grams of Fraction 4, which remained in the alcoholic solution.

	Calculated for $(C_6H_9O_4SO_4)_2Ba$.	Found.		
		Fraction 1.	Fraction 3.	Fraction 4.
Ba	22·1	23·8	23·4	20·2
SO_4	31·2	29·3	—	—
$[\alpha]_D$ for barium salt =		+ 25°	+ 24°	+ 9°
K =		trace	—	36·3

Fraction 4 was heated with phenylhydrazine hydrochloride and sodium acetate, but no osazone was formed. It is evident that the hydrolysis had proceeded to the same stage as in the previous experiment.

d. Thirty Minutes' Hydrolysis of Cellulose-disulphuric acid prepared at 3—5°.—One per cent. of sulphuric acid was employed in this transformation.

14½ grams of barium cellulose-disulphate gave 7·6 grams of barium salt. This is exactly the theoretical yield.

This was fractioned into 4½ grams of Fraction 1 and 3 grams of Fraction 2; Fraction 2 remained in solution in the alcohol. These were again fractioned into Fraction 1*α* and 1*β*, and Fraction 2*α* and 2*β* respectively. On analysis they gave the following numbers.

	Calculated for $[(C_6H_9O_4\cdot SO_4)_2Ba]_5$ $(C_{12}H_{19}O_9\cdot SO_4)_2Ba$.	Found.				
		Fraction 1.		Fraction 1*α*.	Fraction 2.	Fraction 2*β*.
C	25·0	25·3	25·3	—	—	—
H	3·1	3·5	3·8	—	—	—
Ba	20·4	20 4		20·3	16·4	14·9
SO_4	28·6	28·3		26·9	—	—
$[\alpha]_D$ for barium salt =		+ 23°		+ 22°	+ 25°	+ 27°
K =		20·0		20·5	42·4	47·5

Fraction 1 is evidently a pure substance; Fraction 2 is not, but still the amount of impurity is not great. In order to determine if the latter was sugar, the substance was digested with phenylhydrazine hydrochloride and sodium acetate; the small precipitate which was formed was recrystallised from alcohol, and, on examining the crystals under the microscope, it was seen that they were identical with the osazone crystals described above. It is evident that in this transformation a little sugar is formed, the hydrolysis having proceeded a little further than in the two previous experiments.

e. Thirty Minutes' Hydrolysis of Cellulose-disulphuric acid prepared at 15°.—There were obtained 20 grams of Fraction 1, 10 grams of Fraction 2, 7½ grams of Fraction 3, 3½ grams of Fraction 4, and

	Calculated for $[(C_6H_9O_4\cdot SO_4)_2Ba]_3$ $(C_{12}H_{19}O_9\cdot SO_4)_2Ba$.	Found.					
		Fraction 1.		Fraction 2.	Fraction 3.	Fraction 3*α*.	Fraction 5.
C.	26·4	26·71	26·93	—	—	—	—
H	3·4	4·15	4·16	—	—	—	—
Ba....	18·8	19·3		18·7	15·5	17·2	6·4
SO_4 ..	26·4	26·2		25·3	—	22·9	—
$[\alpha]_D$ for barium salt =		+ 72°		+ 69°	—	+ 60°	+ 41°
K =		14·3		14·1	26·8	25·1	63·1

1 gram of Fraction 5, which remained in the alcoholic solution. Fraction 3 was again fractioned into Fraction 3*α* and 3*β*. These gave the numbers at foot of p. 84.

Fractions 1 and 2 are evidently a pure substance; Fraction 3 is not quite pure, but the greater portion is evidently identical with Fractions 1 and 2. The high K and low Ba of Fraction 5 indicate the presence of sugar. In this experiment, as in the previous one, hydrolysis has proceeded sufficiently far to produce sugar.

These experiments indicate that the monosulphuric acid,

$$C_6H_9O_4 \cdot SO_4H,$$

is the limit of the first stage; that is, cellulose-disulphuric acid, $C_6H_8O_3(SO_4H)_2$, hydrolysed by boiling with dilute sulphuric acid, at first only loses sulphuric acid, and yields $C_6H_9O_4 \cdot SO_4H$. On further heating, sugar is formed and more sulphuric acid is lost. The resting point of the action is not well marked, as if the digestion is continued a few minutes too long, or if the percentage of free sulphuric acid is slightly increased, it is carried beyond this point.

The cupric-reducing powers of these barium salts lend additional confirmation to the above, and the optical activities confirm what has been proved with reference to the influence of the temperature at which the original acid is prepared. The following table shows this.

Barium salt.	Temperature at which the original celluloso-disulphuric acid was prepared.	K.	$[\alpha]_D$
$[C_6H_8O_3(SO_4)_2Ba]_2,(C_6H_9O_4 \cdot SO_4)_2Ba$ ..	15°	0	52°
$(C_6H_9O_4 \cdot SO_4)_2Ba$....................	15	10	50
Ditto......................	6	trace	25
$[(C_6H_9O_4SO_4)_2Ba]_5,(C_{12}H_{19}O_9 \cdot SO_4)_2Ba$.	4	20	22
$[(C_6H_9O_4SO_4)_2Ba]_2,(C_{12}H_{19}O_9 \cdot SO_4)_2Ba$.	15	14	70

This shows that neither the barium salts of cellulose-disulphuric acid nor of celluloso-monosulphuric acid reduce Fehling's solution, but that the barium salts of lower acids do; the latter will be more evident later. The optical activities of the barium salts are evidently dependent on the temperature at which the original cellulose-disulphuric acid was prepared.

Hydrolysis of Cellulose-sulphuric acid.—Stage II.

a. Thirty Minutes' Hydrolysis of Cellulose-disulphuric acid prepared at 15°.—Thirty-five grams of cellulose gave 11 grams of Fraction 1, 4½ grams of Fraction 2, and a small amount in the alcoholic solution. Fraction 1 was again fractioned into three portions, Fraction 1*a*, 1*b*, and 1*c*.

	Calculated for $(BaSO_4 \cdot C_{12}H_{18}O_9)_6$ $[Ba(SO_4 \cdot C_6H_9O_4)_2]_3$ $Ba(SO_4 \cdot C_{12}H_{19}O_9)_2$.	Found.			
		Fraction 1.	Fraction 1b.	Fraction 1.	Fraction 2.
C	25·7	—	—	25·8	—
H	3·2	—	—	3·76	—
Ba	22·6	22·6	22·5	—	21·5
SO_4	23·8	23·8	24·0	-	22·9
$[\alpha]_D$ for barium salt	+ 60°	—	—	+ 54°	
K =	4·9	3·8	—	6·3	

These numbers indicate that we are here dealing with a pure substance. Sugar was also formed in the transformation, but it was not examined.

b. One Hour's Hydrolysis of Celulose-disulphuric acid prepared at 15°.—A cellulose-sulphuric acid obtained by 30 minutes' hydrolysis, and shown to be $C_6H_9O_4 \cdot SO_4H, C_{12}H_{19}O_9 \cdot SO_4H$, was digested at 100° for 30 minutes with 2 per cent. sulphuric acid; 25 grams of the original barium salt gave 2 grams of Fraction 1, 5 grams of Fraction 2, 0·3 gram of Fraction 3, 2 grams of Fraction 4, 6 grams of Fraction 5, 3 grams of Fraction 6, and an alcoholic solution which contained Fraction 7, amounting to 2 grams. Fraction 2 was again fractioned into two equal parts, Fraction 2*a* and 2*b*.

	Calculated for $(BaSO_4C_{12}H_{18}O_9)_2$. $(BaSO_4 C_{12}H_{19}O_9)_2$.	Found.			
		Fraction 1.	Fraction 2.	Fraction 2b.	Fraction 7.
Ba	19·8	20·4	19·0	19·4	2·8
SO_4......	19·1	18·6	19·0	18·9	—
$[\alpha]_D$ for barium salt		—	+ 60°	+ 63°	+ 57·8°
K =		16·5	14·0	11·8	78·1

Fraction 2 is evidently a pure substance, and Fraction 1 is practically the same.

A portion of Fraction 7, amounting to 1·5 grams, was digested at 100° for two hours with 4 grams of phenylhydrazine hydrochloride and 6 grams of sodium acetate dissolved in 30 c.c. of water; the yellow osazone which separated weighed 1 gram. After recrystallisation from alcohol, it was found to melt at 194°; a comparative experiment with dextrosazone gave m.p. 205°.

It is evident that we have here the same sugar as in the other transformations described. All attempts to crystallise it failed.

c. One and a Half Hours' Hydrolysis of Cellulose-disulphuric acid prepared at 13°.—Eighty grams of cellulose were converted into cellulose-sulphuric acid at 13°. This was digested with 2 per cent. sulphuric acid at 100° for 1½ hours. The neutralised solution, after being filtered and concentrated, was precipitated by alcohol, and the precipitate fractioned into 10 grams of Fraction 1, 20 grams of

Fraction 2, 10 grams of Fraction 3, 5 grams of Fraction 4. Fraction 3 was again fractioned into Fractions 3*a*, 3*b*, and 3*c*. The alcoholic solution was concentrated in a vacuum nearly to dryness, and the residue dissolved in methylic alcohol (sp. gr. 0·820). This solution was precipitated by absolute alcohol in two fractions, 2½ grams of Fraction 5*a*, 3 grams of Fraction 5*b*; the alcoholic solution was precipitated by ether in two fractions, namely, 3 grams of Fraction 6, 2½ grams of Fraction 7; and the ether-alcohol solution contained 2½ grams of Fraction 8.

The fractions were analysed as follows.

Calculated for $C_{12}H_{19}O_9SO_4Ba$	Ba.	SO_4.	$[\alpha]_D$.	K.
$[(C_{12}H_{19}O_9SO_4)_2Ba]_2$	16·9	19·9	—	—
Fraction 1....	16·6	19·1	+60°	8·9
„ 2....	16·1	19·0	+59	10·0
„ 3....	14·3	19·3	+58	14·5
„ 3*a* ..	15·4	18·8	+55	12·4
„ 3*b*...	14·7	19·5	+57	13·9
„ 5*a* .	10·7	—	+25	40·6
„ 5*b*...	11·1	—	+25	45·8
„ 6....	11·2	12·0	+21	47·0
„ 7....	9·0	—	+15	55·9
„ 8....	10·9	—	0	51·0

Fractions 1 and 2 are evidently a pure substance; Fraction 3 is not, but a portion of it is identical with Fractions 1 and 2.

Fractions 5*a*, 5*b*, and 6 are also pure substances. The high K suggested the presence of sugar. 1 gram each of Fraction 5*b* and Fraction 6 was digested with phenylhydrazine acetate for one hour.

1 gram of Fraction 5*b* gave 0·8 gram of crude osazone.
1 „ „ 6 „ 0·7 „ „ „

The osazone was recrystallised from alcohol, and was found to be identical with that previously obtained; m. p. 193°.

We have here a substance which behaves with phenylhydrazine as if it contained sugar, but yet sugar cannot be separated from it. The hydrolysis appears to have proceeded within the complex molecule without sugar having been actually split off. It is evident that a similar product is formed in the other transformations described. In order to obtain the sugar, it is probably necessary to hydrolyse the whole of the cellulose-sulphuric acid. This requires such a prolonged digestion as also to destroy a great portion of the sugar, and explains the small quantity obtained by Flechsig, and by Lindsey and Tollens.

d. Two Hours' Hydrolysis of Cellulose-disulphuric acid prepared

The mean molecular weight is $\frac{6 \times 539 + 5 \times 619 + 863}{12} = 598$.

This is exactly double the molecular weight found which we might expect for a salt.

Expt. II.—Molecular weight of

$$C_{12}H_{18}O_9BaSO_4,2(C_{12}H_{19}O_9 \cdot SO_4)_2Ba.$$

4·626 grams dissolved in water made up to 50 c.c.
Sp. gr. of solution 1·04463.
Freezing point of water − 0·14°.
Freezing point of solution − 0·83°.
Molecular weight $= \frac{20 \times 4{\cdot}626 \times 100}{0{\cdot}69 \times 47{\cdot}605} = 282$.
Molecular weight of $C_{12}H_{18}O_9BaSO_4 = 539$.
Molecular weight of $(C_{12}H_{19}O_7 \cdot SO_4)_2Ba = 863$.
Mean molecular weight is $\frac{539 + 2 \times 863}{3} = 755$.

This is rather more than twice, but less than three times, the molecular weight found.

As might be expected in a research of this kind, a great number of experiments had to be made. Those here described form only a portion. The others do not add anything further to our knowledge, and it is unnecessary to record them.

In conclusion, I wish to express my deep gratitude to Mr. C. O'Sullivan, F.R.S., for the kind encouragement which he has given to me during the progress of this work.

Burton-on-Trent.

XI.—*Note on the Interaction of Bismuth Haloïd Compounds and Hydrogen Sulphide.*

By M. M. Pattison Muir, M.A., and Edwin M. Eagles, B.A., St. John's College, Cambridge.

In 1854, Schneider (*Ann. Phys. Chem.*, 1854, **93**, 64) obtained BiSCl by passing hydrogen sulphide over the double compound,

$$BiCl_3,3NH_4Cl,$$

kept hot; also by heating this same double chloride with sulphur, and by causing it to react with bismuth sulphide. He (*Ann. Phys. Chem.*, *loc. cit.*, and **110**, 147) likewise prepared BiSI by heating bismuth sulphide and iodine, mixed in the ratio $Bi_2S_3 : 6I$; also by adding bismuth sulphide to hot bismuth iodide, and by subliming a mixture of bismuth sulphide, sulphur, and iodine.

In 1881 (Trans., 1881, **39**, 33), one of us, in conjunction with Hoffmeister and Robbs, obtained indications of the formation of bismuth thiobromide by heating a mixture of bismuth bromide and sulphur; it was also shown in the paper referred to that bismuth iodide and sulphur do not combine when heated together.

Hydrogen sulphide and bismuth chloride, and hydrogen sulphide and bismuth bromide, interact at the ordinary temperature, forming brownish-red solids, and evolving acid fumes; the actions are hastened by gently warming the bismuth haloids from time to time, and constantly shaking, so as to expose fresh portions of the solids to the action of the gas. By continuing the passage of dried hydrogen sulphide as long as any acid-smelling fumes were given off when the solids were heated to very low redness, then removing excess of hydrogen sulphide by a current of dry carbon dioxide, shaking the products with very dilute, cold hydrochloric acid until bismuth ceased to be detected in the washings, washing with cold water, and drying at 100°, we obtained greyish-red, crystalline, non-deliquescent powders, which gave results, on analysis, agreeing with the formulæ BiSCl and BiSBr respectively. We append some of the results of our analyses:—

	Calculated for BiSCl.	Found.		
Bismuth	75·50	75·00;	75·14;	75 18
Sulphur	11·62	12·13		
Chlorine	12·88	13·06		
	100·00	100·19		

	Calculated for BiSBr.	Found.	
Bismuth	64·30	64·84	
Sulphur	9 89	9·45	
Bromine	25 81	26·16	25·95
	100 00	100·45	

When the greyish-red products of the interaction of hydrogen sulphide with bismuth chloride or bismuth bromide, at a very low red heat, were heated to full redness in a stream of dried hydrogen sulphide, acid-smelling fumes were given off, and grey, crystalline solids remained, which contained only bismuth and sulphur.

Estimations of bismuth showed that bismuth sulphide, Bi_2S_3, was produced in both cases.

Analyses of the products of the interaction of bismuth chloride, or bismuth bromide, and hydrogen sulphide, at temperatures varying from the ordinary temperature to very low redness, showed that in every case the only solid products were BiSCl and BiSBr respectively.

Bismuth sulphide, prepared by precipitation and dried at 100°, interacts with chlorine at the ordinary temperature, bismuth chloride subliming, and a gas, smelling of sulphur chloride, being given off. By gently warming the bismuth sulphide and continuing to pass chlorine over it as long as any action occurred, we obtained a greyish-red solid, which, after washing with very dilute, cold, hydrochloric acid, and then with cold water, and drying at 100°, was exactly similar to bismuth thiochloride, and was found to contain 75·21 per cent. of bismuth; BiSCl requires 75·50 per cent. bismuth. A similar result was obtained by passing bromine vapour over bismuth sulphide. The action began at once; after gently warming in bromine vapour as long as the action continued, a greyish-red solid remained containing 64·51 per cent. of bismuth; BiSBr requires 64·30 per cent. bismuth.

We did not succeed in preparing a bismuth thio-iodide by heating bismuth iodide in a stream of hydrogen sulphide; bismuth iodide sublimed, and a steel-grey, crystalline solid remained at the bottom of the small flask; this was powdered, and again heated in dried hydrogen sulphide, when a steel-grey residue was left. Both the sublimate and the grey residue contained bismuth and iodine only; the percentage of bismuth was 35·40; BiI_3 requires 35·31 per cent. of bismuth.

We then attempted to prepare a thio-iodide by the interaction of bismuth sulphide and iodine, mixed in the ratio $Bi_2S_3 : 6I$. A reaction occurred when the substances were rubbed together in a mortar; a little iodine sublimed, and a steel-grey solid remained. When this dark-coloured, solid mass was powdered and heated, almost the whole of it sublimed, and the sublimate was proved to be bismuth iodide; the steel-grey residue was also found to be bismuth iodide. Hence the interaction of bismuth sulphide and iodine may be expressed, with fair accuracy, by the equation

$$Bi_2S_3 + 6I = 2BiI_3 + 3S.$$

Bismuth thio-iodide, BiSI, was obtained, but not free from bismuth sulphide, by heating a mixture of bismuth sulphide and bismuth iodide, approximately in the ratio $Bi_2S_3 : BiI_3$. A little bismuth iodide sublimed; the residue was powdered, again heated, and then washed with cold dilute hydrochloric acid (about 1 : 10) as long as bismuth went into solution. After washing with water and drying at 100°, the steel-grey, crystalline solid that remained was found to contain 33·9 per cent. of iodine and 9·08 per cent. of sulphur; BiSI requires 34·6 per cent. of iodine and 8·72 per cent. of sulphur. Three determinations of bismuth gave 62·7 per cent., 61·06 per cent., and 59·1 per cent.; BiSI requires 56·86 per cent. of bismuth. The substance was almost certainly BiSI containing a little Bi_2S_3; it contained no free iodine, nor was bismuth iodide removed from it by treatment with boiling alcohol.

The chief results of our experiments may be expressed with tolerable exactness in the following equations :—

(1.) $BiX_3 + xH_2S = BiSX + 2HX + (x-1) H_2S$; at temperatures up to a very low red heat.

(2.) $2BiX_3 + xH_2S = Bi_2S_3 + 6HX + (x-3) H_2S$; at a full red heat.

In equations (1) and (2) $X = Cl$ or Br.

(3.) $BiI_3 + xH_2S$; no reaction up to a full red heat.

(4.) $Bi_2S_3 + xCl = BiSCl + BiCl_3 + S_2Cl_2 + (x-6) Cl$; at a low red heat.

(5.) $Bi_2S_3 + xBr = BiSBr + BiBr_3 + 2S + (x-4) Br$; at a low red heat.

(6.) $Bi_2S_3 + xX = 2BiX_3 + 3S + (x-6) X$; at a full red heat $X = Cl$ or Br.

(7.) $Bi_2S_3 + 6I = 2BiI_3 + 3S$; at a very low red heat.

(8.) $xBi_2S_3 + BiI_3 = 3BiSI + (x-1) Bi_2S_3$; at a low red heat. x nearly equal to 1.

Note on the Method used for Analysing Bismuth Thiohaloid Compounds.

After several trials, we found the following method very satisfactory. A weighed quantity of the thiohaloïd compound was digested, at about 70°, with a large excess of solid silver nitrate and concentrated (not fuming) nitric acid, in a bottle closed by a ground glass plate which was clamped on to the top of the bottle. After about an hour's digestion, the bottle was cooled, and the contents were washed out into a beaker, water was added, and the liquid was heated. The silver haloïd was treated in the ordinary way. Excess of silver was removed by boiling down with hydrochloric acid; bismuth was precipitated from the filtrate by adding ammonia and ammonium carbonate solution; and barium sulphate was precipitated from the filtrate in the usual manner.

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XII.—*The Constituents of* Piper ovatum.

By Wyndham R. Dunstan, M.A., F.R.S., and Henry Garnett.

This plant (*Piper ovatum* Vahl, or *Ottonia Vahlii*) grows in the West Indies, and is briefly described in Grisebach's "Flora of the West Indies," (p. 172).

It has been examined in this laboratory, at the suggestion of Mr. W. T. Thiselton Dyer, F.R.S., the Director of the Royal Gardens, Kew, who received it from Mr. John H. Hart, F.L.S., the Superintendent of the Royal Botanic Garden, at Trinidad, to whom we are indebted for a further supply of the material. The plant somewhat resembles Jaborandi in appearance, and has been employed in Trinidad as a remedy for snake bite, and as a cure for hydrophobia in animals. When chewed, it gives rise to a persistent tingling of the tongue and lips, which is followed by a sensation of numbness, accompanied by profuse salivation, in these respects recalling pellitory. Some irritation at the back of the throat is also observed. All parts of the plant—leaves, stem, and root—possess this property, but the leaves and root appear to act more powerfully than the stem; the leaves have an aromatic taste due to an essential oil which is absent from the root.

The following is a brief botanical description of *Piper ovatum*, taken partly from Grisebach and partly from our own observations.

Shrub, 2—4 feet high; root woody, spreading. Stems erect, slender, somewhat woody, branching in zig-zags, nodes tumid; leaves alternate, 3—6 inches long, 2—3 inches broad, ovate, pointed, broadly cuneate at base, papery opaque, glabrous; petiole channelled, naked, about ⅛—¼ inch long. Flowers usually racemose, pedicles jointed with the flower. Bracts cucullate, usually at the base of a pedicel; stamens 4 (—3) inserted round the ovary; stigmas 4, sessile. Pericarp baccate, tetragonal. Berries pedicellate, somewhat longer than their pedicel, rounded at base, mucronate with a bluntish point. Habitat, Trinidad.

A number of the living plants have been brought to England, in Wardian cases, and are at present growing at Kew Gardens, but so far they have shown no signs of flowering.

Volatile Constituents.

As the aromatic taste of the leaves suggested the probability of the presence of a volatile oil, the leaves were distilled with steam in the usual manner and the distillate extracted with ether. By this means a small quantity of an almost colourless, volatile, aromatic oil was obtained which was non-alkaloïdal and did not produce any tingling of the tongue. When cooled below 0° and stirred, the oil showed no tendency to solidify. Its density was 15°/15° = 0·9904. It boiled at about 245°, nearly the whole passing over between 240° and 250°. It appears to be optically inactive, since a 6 per cent. solution in alcohol produced no rotation of the polarised ray. When dry hydrogen chloride was led into a dry ethereal solution of the oil, there was no separation of crystals, even after the liquid had been cooled to —13°. When a drop of the oil was dissolved in chloroform and strong sulphuric acid added, an intense crimson coloration was produced, passing into a reddish-violet. Aqueous alkalis did not act on the oil, and it formed no compound with sodium hydrogen sulphite. We have not had sufficient of the substance for analysis, but from the properties recorded above the volatile oil of *Piper ovatum* would appear to be a *sesquiterpene*. The leaves contain this oil to the largest extent, little or none being present in the root or stem.

Non-volatile Constituents.

The liquid remaining with the leaves after distilling off the oil with steam, though highly coloured, had none of the activity of the leaves themselves, and gave rise to little or no tingling when tasted; it was, therefore, clear that the active constituent was not appreciably soluble in water. This aqueous solution contained no alkaloïd, but a *sugar* having cupric reducing power was present, and also a considerable quantity of *potassium nitrate*. The leaves having been drained from the water were digested for some hours with boiling alcohol (50 per cent.), the process being repeated until they had lost nearly all their tingling property. The green alcoholic solution, which was highly active, was evaporated to dryness, the residue extracted with absolute alcohol, and the alcoholic solution fractionally precipitated by the addition of small quantities of water aided by the evaporation of some of the alcohol. The first precipitate contained nearly the whole of the chlorophyll, but scarcely any of the active constituent. The second precipitate also contained chlorophyll, but was active although not nearly so strongly as the filtrate; this second precipitate was, therefore, dissolved in alcohol and reprecipitated by water, the filtrate being added to the original filtrate, and the whole evaporated until the alcohol had been dissipated. The aqueous solution was then extracted by shaking with ether which removed the active constituent together with colouring matter. The residue left on evaporating the ether was dissolved in alcohol, and the solution fractionally precipitated with water, this process being repeated until the whole of the green colouring matter had been removed. Ether then extracted from the liquid, after the evaporation of the alcohol, a light brown resin which was highly active in inducing tingling of the tongue and showed no signs of crystallisation even after prolonged standing.

The similarity in the physiological action of *Piper ovatum* to that of the medicinal pellitory has already been noticed, and in the latter case the action is usually attributed to a resin, about the properties of which, however, little is known.* The resin obtained from *P. ovatum* was fully examined in the hope of separating some crystalline active substance from it. It was soon found that the resin was not a single substance, in spite of the long process of purification to which it had already been submitted. It was further purified by dissolving it in ether, and fractionally precipitating the ethereal solution with light petroleum, in which the active constituent is nearly insoluble; by this means, it was obtained lighter in colour but still resinous. The resin was again dissolved in ether, and the solution shaken with weak aqueous ammonia, which removed a further quantity of inactive material. After the ethereal solution had been dried with calcium chloride, a resin, which was quite inactive, separated from the liquid.

The ethereal solution, when spontaneously evaporated, left a highly active substance which, however, was still resinous, and refused to crystallise. The resin was next dissolved in alcohol, and the solution fractionally precipitated by the addition of water; the first fraction was resinous and nearly inactive, the later fractions were lighter in colour than the first and highly active. On repeating the process on the later fraction, a bulky but very light mass of feathery crystals separated, which were nearly colourless and more active than any substance previously obtained. This material was, with difficulty, recrystallised several times from dilute alcohol, and lastly from hot, light petroleum. A further quantity was obtained from the purified resin by shaking the ethereal solution with ammonia, dissolving the residue in alcohol, and precipitating the solution with light petroleum, the precipitate being again dissolved in alcohol and reprecipitated with petroleum until it was capable of crystallising.

As will be inferred from the details which have been given, the separation of this crystalline active substance from the colouring matter, fat, wax, and resin which so obstinately adhere to it proved to be a very tedious operation, especially troublesome when the object was to obtain a sufficient quantity for analysis. Much time was spent in trying various methods of extracting the substance from the plant, and in purifying the product; the most successful plan was found to be the following, which, however, is still long and laborious.

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* See the following paper.

The dried and finely-powdered material (leaves, root, and stem, all of which contain the active constituent) is repeatedly extracted with hot, light petroleum (boiling below 80°) until the active substance is almost entirely removed; the removal of the last traces is very troublesome. The active constituent is not readily soluble in light petroleum, but it is found to be advantageous to use this liquid because it removes a smaller quantity of other substances than is the case with better solvents of the active constituent, such as alcohol, ether, chloroform, or acetone, which dissolve so much colouring matter, resin, and fat that the subsequent purification of the active substance is very much lengthened.

The greater part of the light petroleum is distilled from the solution, and the residue is well shaken with alcohol (60 per cent.). By repeating this operation several times, nearly the whole of the active constituent passes into the alcohol, whilst most of the colouring matter, fat, essential oil, &c., remains in the layer of petroleum. On concentrating the dilute alcoholic solution, a considerable quantity of semi-crystalline active substance separates along with green colouring matter; this is partially purified by repeated crystallisation from dilute alcohol. By this means much of the resin, which so obstinately clings to it, is removed, and more is separated by shaking an ethereal solution with dilute aqueous ammonia. The dried ethereal solution may then be precipitated by the addition of small quantities of light petroleum, which throws out the resin in the first fraction, whilst the later fractions are crystalline and consist of the nearly pure active constituent. Finally, the substance is recrystallised by adding dry ether to its solution in absolute alcohol, and allowing the solution to evaporate spontaneously. The crystals which separate are dried on a tile in the air or in a desiccator; at 100° a little decomposition occurs, and the crystals become slightly yellow.

The preparation of sufficient material for analysis occupied a very long time, since the best process for isolating it is rather wasteful, as some of the active constituent is thrown down along with the resin during the fractional precipitation, and requires a succession of similar operations in order to recover it. Although we have used about 12 kilos. of the plant, we were not able to prepare more than about 2 grams of the pure active constituent. In all probability the plant does not contain as much as 0·1 per cent. of this substance, but it exerts so powerful a physiological action that from the effect produced by chewing the leaves or root one is led to expect a far larger proportion.

Properties and Composition of the Active Constituent, Piperovatine.

When pure, the active constituent forms colourless, light needles which often crystallise in rosettes. In appearance, these somewhat resemble the alkaloïd caffeïne, and melt at 123° (corr.), decomposing slightly. The substance is nearly insoluble in water, very sparingly soluble in light petroleum, and not much more so in dry ether. It dissolves readily in alcohol, chloroform, and acetone. The solution of the highly purified substance in strong alcohol has the curious property of apparently gelatinising when water is added to it in just sufficient quantity to cause precipitation; the dissolved substance being thrown out in a bulky mass of microscopic crystals resembling a jelly. On this account it is difficult to obtain it in well-defined crystals, but this may be managed by adding dry ether to the solution in absolute alcohol, and allowing the liquid to evaporate spontaneously. The substance appears to be optically inactive; an alcoholic solution containing 1·5 per cent. did not rotate the polarised ray. The compound contains carbon, hydrogen, nitrogen, and oxygen. Several combustions have been made with different specimens of the material, with the following results.

I. 0·1054 gave 0·2813 CO_2 and 0·0858 H_2O. C = 72·78; H = 9·04.
II. 0·2023 „ 0·5335 „ „ 0·1484 „ C = 71·92; H = 8·15.
III. 0·1847 „ 0·4982 „ „ 0·1391 „ C = 73·56; H = 8·37.
IV. 0·1775 „ 0·4810 „ „ 0·1356 „ C = 73·90; H = 8·49.

Of these four combustions, III and IV were made with the purest specimens, and give as a mean composition C = 73·73, H = 8·43 per cent., the percentage of nitrogen (determined by the absolute method) was 5·96. These data agree well with those calculated from the formula $C_{16}H_{21}NO_2$, which requires C = 74·13; H = 8·10; N = 5·40 per cent. The active constituent exhibits, therefore, the composition of a vegetable alkaloïd, and shows some resemblance to piperine ($C_{17}H_{19}NO_3$), the alkaloïd of pepper, a plant belonging to the same natural order.

Piperine has very feebly basic properties, and forms salts which are very unstable. The substance from *Piper ovatum*, to which we propose to assign the name *piperovatine*, is devoid of basic properties, being nearly insoluble in dilute acids, and therefore, from this point of view, does not come within the usual definition of an alkaloïd. Nevertheless, further investigation will probably show that its constitution is precisely similar to that of such alkaloïds as piperine, atropine, and aconitine, that is to say, it would seem from our observations to be composed of a basic pyridine nucleus (*e.g.*, piperidine), associated with an acid radicle, the acidity of the radicle exactly neutralising the basic power of the other residue, so that the resulting derivative is neither basic nor acidic.

Piperovatine dissolves in glacial acetic acid, but may be precipitated unchanged by the addition of water. It is insoluble in dilute hydrochloric acid and in dilute sulphuric acid; on boiling it with these acids, hydrolysis appears to take place, and the solution now gives the reactions of an alkaloid, but we have not obtained sufficient of the product for identification. It appears, however, to be a pyridine derivative, and to present some analogies to piperidine; there would seem to be also an acid product of hydrolysis, but this we have never obtained except in traces.

Piperovatine is also devoid of acid properties. It does not dissolve in weak alkalis. Strong alkalis such as potash, especially when warm, appear to hydrolyse it, quickly forming the acid and the pyridine base referred to above.

Its decomposition products require a fuller examination than we have been able to subject them to with the small quantity of material at our disposal.

Physiological Action of Piperovatine.

The physiological action of piperovatine has been investigated for us by Professor Cash, F.R.S., of Aberdeen. He finds it to act as a temporary depressant of both motor and sensory nerve fibres, and also of sensory nerve terminations, producing some local anæsthesia. It acts as a heart poison, and also as a powerful stimulant to the spinal cord (in frogs), causing a tonic spasm somewhat resembling that produced by strychnine.

A 2·5 per cent. solution (in almond oil) produced no anæsthetic effect when rubbed on the skin, and it has been found generally to possess but little penetrative power, at all events in the form of this solution. When, however, the same solution is applied to the tongue, moderate local anæsthesia is produced, accompanied by a feeling of numbness and coldness, and much salivation.

In attempting to utilise the local anæsthetic effect of piperovatine, the want of penetrating power, the temporary character of its action, and, above all, its property of causing salivation, have interfered with its successful employment in the minor operations of dentistry. The solution of piperovatine in almond oil has, however, given promising results in affording temporary relief in painful superficial lesions.

It would therefore seem to be worth while to follow up in therapeutic trials the analogies, suggested by these preliminary experiments, of the physiological action of piperovatine to that of strychnine, cocaïne, pilocarpine, and piperine. It is also clear that the action of piperovatine is very similar to that of the medicinal pellitory, the *Anacyclus Pyrethrum* of the Pharmacopœia, and it might be useful to determine how far this similarity can be traced, and also whether *Piper ovatum* or its alkaloïd piperovatine could be used medicinally in the place of pellitory.

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XIII.—*Note on the Active Constituent of the Pellitory of Medicine.*

By Wyndham R. Dunstan, M.A., F.R.S., and Henry Garnett.

The success which attended our attempt to separate a crystalline, physiologically active substance from the "resin" of *Piper ovatum*, led us to examine the "resin" which is usually regarded as the active constituent of *Anacyclus Pyrethrum*, the root of which is used in medicine under the name of "Pellitory." As has been pointed out in the preceding paper on *Piper ovatum*, there is a strong resemblance between the physiological action of these two drugs, both producing, when chewed, a persistent tingling and partial insensibility of the tongue and neighbouring surfaces, accompanied by profuse salivation.

In 1876, Buchheim (*Archiv. Exper. Pathol.*, 5, 458) separated a crystalline material from pellitory, which he regarded as its active constituent and named "pyrethrine." The properties of this substance were not fully described, and no analysis of it was made, nor were its physical constants recorded. Buchheim classed it with the piperine group because, on hydrolysis, it furnished what seemed to be piperidine and an organic acid, but here again the investigation was left in a very incomplete state. Owing, apparently, to their fragmentary character, Buchheim's observations are not even referred to in many of the standard treatises on pharmacology and materia medica, the statements of the older workers as to the resinous character of the active constituent of pellitory being accepted as correct.

This being the present state of knowledge of the active principle of pellitory, we decided to examine this drug, and determine whether its physiological action was due to a crystalline substance, closely allied to, if not identical with, piperovatine.

Our first experiments furnished an amorphous, highly active resin, from which no crystalline material could be separated; but, after preparing a considerable quantity of this "resin" and submitting it to a process of repeated fractionation, we ultimately obtained a crystalline, physiologically active substance, capable of producing effects very similar to those caused by piperovatine. This substance, like piperovatine, with which, indeed, it may in the end turn out to be identical, has neither basic nor acidic properties. In its behaviour towards solvents, it also closely resembles piperovatine, but, since the purest specimen we have been able to prepare shows certain points of difference as compared with the product from *Piper ovatum*, we propose provisionally to name it *pellitorine*. It is very probable that it is the same substance as that isolated, but very imperfectly examined, by Buchheim, in 1876, and named by him *pyrethrine*. Since, however, this name has also been used to designate the supposed resinous active constituent of pellitory, confusion will be avoided by speaking of the alkaloïd we have separated as "pellitorine."

The process we have adopted for isolating pellitorine from pellitory root is very similar to that which we have described in the previous paper in connection with the separation of piperovatine from *Piper ovatum*, and it is not any less tedious. The main steps are as follows.

The finely-powdered pellitory root (15 kilos.) was almost exhausted of its active constituent by extraction with strong alcohol. The dark yellowish-brown solution was then distilled, and nearly all the alcohol recovered. The dark, viscid liquid which remained was repeatedly shaken with ether, which removed the whole of the active constituent, together with a considerable quantity of colouring matter. The ethereal solution was next shaken with a solution of sodium carbonate (10 per cent.), which dissolved a good deal of resin and colouring matter, leaving the active constituent in the ether. The residue left on evaporating the ether was a brown resin, which, however, deposited some rosettes of needle-shaped crystals after prolonged standing in a desiccator. These crystals closely resembled those obtained from *Piper ovatum*, and were highly active. More crystals were obtained by adding light petroleum to some of the ethereal solution, some inactive resin being separated as a first fraction. A few more crystals were also obtained by dissolving the resinous residue of the ethereal solution in alcohol and fractionally precipitating it with water, as described in our foregoing paper in connection with the purification of piperovatine. Pellitory root, however, contains so much resin that the separation of the crystalline pellitorine is a very difficult matter, and, so far, we have not obtained more than enough to enable us to compare its chief properties with those of piperovatine. In crystalline form, as well as in physiological action, there is a very close resemblance, and the solubility of the two substances appears to be about the same.

Both are free from basic and acidic properties; pellitorine does not dissolve in dilute acids, and, although it is soluble in glacial acetic acid, it is, like piperovatine, precipitated unchanged on adding water. Boiling dilute acids appear to slowly hydrolyse pellitorine as they do piperovatine, and also to give rise to what is apparently a pyridine derivative possessing basic properties, which Buchheim suggested might be piperidine. We have observed that what is apparently this same base is present to a small extent in pellitory root. Pellitorine is insoluble in dilute alkalis, but strong potash solution gradually decomposes it, forming a base like that produced in the acid hydrolysis. The experiments we have made with the small quantity of pellitorine at our disposal lead us to conclude, however, that pellitorine is not so readily decomposed by alkalis as piperovatine. Moreover, we have not been able to observe the curious gelatinisation of pellitorine which is so marked when water is added to a strong alcoholic solution of piperovatine.

Pellitorine deserves a very full examination, not only because of its remarkable physiological action, but also on account of the close relationship to piperine and to piperovatine, which the results of our preliminary examination so strongly suggest. We had hoped to be able to pursue this subject, but, as the interruption of our joint work may prevent this, we have thought it desirable to put on record the facts we have ascertained with reference to the nature of the active principle of pellitory and its relation to that of *Piper ovatum.*

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XIV.—*Action of certain Acidic Oxides on Salts of Hydroxy-acids.* Part I. *Metallic Tartrarsenites.*

By G. G. Henderson, D.Sc., M.A., Professor of Chemistry in the Glasgow and West of Scotland Technical College, and A. R. Ewing, Ph.D.

It is usually stated in works of reference that some so-called double tartrates of the same type as tartar emetic, but containing arsenic in place of antimony, have been prepared; reference to original sources, however, shows that only one of those compounds has been investigated with any degree of thoroughness. Mitscherlich, by dissolving arsenious oxide in a solution of ammonium hydrogen tartrate, obtained a compound to which he ascribed the formula $NH_4(AsO)C_4H_4O_6.\frac{1}{2}H_2O$, and the same substance was prepared by Werther (*J. pr. Chem.*, **32**, 409) and by Marignac (*Ann. des Mines*,

[5], **15**, 288), who showed it to be isomorphous with tartar emetic. Marignac also attempted to prepare a similar tartrate of potassium and arsenic, but only obtained a small quantity of a crystalline substance which he did not analyse. Pelouze (*Annalen*, **44**, 100) made a somewhat similar experiment with arsenic acid, in a boiling solution of which he dissolved potassium hydrogen tartrate; on adding alcohol, a white crystalline powder, to which he gave the formula

$$K(AsO_2)C_4H_4O_6,2\frac{1}{2}H_2O,$$

was precipitated. Lastly, in a paper recently published by Adam (*Compt. rend.*, **118**, 1274), it is stated that arsenious acid gives with potassium sodium tartrate, as with potassium hydrogen tartrate, "the arsenious emetic of Mitscherlich."

In the course of an investigation of the compounds formed by the interaction of acidic oxides and salts of various hydroxy-acids, we have prepared several compounds of the type of tartar emetic, but with arsenic in place of antimony; the present paper contains an account of these substances.

Arsenious oxide dissolves readily in hot solutions of sodium hydrogen tartrate, and interaction occurs according to the equation $As_2O_3 + 2NaHC_4H_4O_6 = H_2O + AsO{\cdot}NaC_4H_4O_6$. In order to prepare this *sodium tartrarsenite*, of which the formation is represented in the above equation, the calculated quantity of finely-powdered arsenious oxide is added to a boiling solution of sodium hydrogen tartrate, and after heating for about 15 minutes longer, the almost clear solution is filtered and evaporated to a small bulk. On cooling, the salt crystallises out as a mass of delicate silky needles; these are collected and washed with a little cold water. A further crop of crystals may be obtained from the mother liquor by the addition of alcohol. The salt is purified by recrystallisation from water or from dilute (50 per cent.) alcohol. From the former solvent, it separates in well-developed aggregates of needles or prisms, from the latter in colourless plates.

Analysis showed the formula to be $AsO{\cdot}NaC_4H_4O_6,2\frac{1}{2}H_2O$.

	Calculated.	Found.
As	24·43	24·72
H_2O	14·66	14·78

The salt becomes anhydrous if heated at 105°, or by exposure in a vacuum over sulphuric acid. It is quite stable when in the solid state, and may even be heated for several hours at temperatures approaching 200° without undergoing decomposition. It has a rather sweet, not unpleasant taste, is highly poisonous, and is easily soluble in water, but insoluble in alcohol.* The aqueous solution is acid, and decomposes sodium carbonate with effervescence, but whenever the neutral point is reached decomposition occurs, arsenious oxide being precipitated and normal sodium tartrate left in solution. The same effect is produced if an aqueous solution of the salt is neutralised with caustic soda.

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* Professor Charteris, of Glasgow University, informs us that he finds the

The corresponding *ammonium* salt (the only compound of this series previously described) was found to have the composition assigned to it by Mitscherlich, namely, $AsO(NH_4)C_4H_4O_6,\frac{1}{2}H_2O$, as it gave the following figures on analysis. Arsenic, found, 28·29 per cent.; calculated, 28·19 per cent. It is easily prepared in the same way as the sodium salt, and can be purified by recrystallisation from dilute alcohol, from which it separates in small, glistening needles readily soluble in cold water. The salt is less stable than the sodium salt, as when it is kept for some time the crystals lose their transparency and crumble down, and if then treated with water they are found to have decomposed to some extent into arsenious oxide and ammonium hydrogen tartrate.

Potassium tartrarsenite is much more difficult to prepare, owing to its great instability in aqueous solution; this instability is doubtless the result of the tendency to form the sparingly soluble potassium hydrogen tartrate, though it is remarkable that the ammonium salt is so much more stable, considering that ammonium hydrogen tartrate is also sparingly soluble in water. The salt was finally obtained by adding arsenious oxide in small quantities at a time to a boiling concentrated solution of potassium hydrogen tartrate until no more was dissolved, filtering the hot liquid, allowing it to cool, and then adding two volumes of alcohol. A finely crystalline, white powder quickly separated, and was at once collected, washed with alcohol, and dried on a porous plate. After 12 hours' standing, the alcoholic mother liquor deposited long, silky needles. Analysis showed that the composition of the needles was practically the same as that of the precipitate, and the results agreed fairly well with those calculated for the formula $AsOKC_4H_4O_6,H_2O$.

	Calculated.	Found.
As	25·34	25·75
H_2O	6·08	6·23

When potassium tartrarsenite is treated with water it is quickly decomposed, even in the cold, yielding potassium hydrogen tartrate and arsenious oxide. It crystallises in long needles from dilute alcohol, but apparently undergoes slight decomposition in the process.

physiological action of sodium tartrarsenite to be practically the same as that of *Liq. arsenicalis;* it is therefore probable that the salt may find applications in medicine.

The well-characterised *barium* salt, $Ba(AsOC_4H_4O_6)_2,H_2O$, is thrown down as a heavy, white, crystalline precipitate when concentrated solutions of barium chloride and of the sodium salt are mixed. It is only slightly soluble in hot water, and cannot well be recrystallised, because, like the other salts of this series, it is partially decomposed when treated with much boiling water. It can be obtained in the crystalline condition, however, by mixing dilute solutions of barium chloride and of the sodium salt, when it is gradually deposited in the form of delicate, lustrous needles. The analytical results were as follows.

	Ba.	As.	H_2O.
Calculated....	21·64	23·69	2·84
Found	21·55	23·00	3·16

The corresponding *strontium salt* is prepared in like manner, but as it is much more soluble than the barium salt, concentrated solutions must be used. It separates in small, transparent crystals, and is much more unstable than the barium salt. Its composition is represented by the formula $Sr(AsOC_4H_4O_6)_2,H_2O$. (Arsenic, found, 25·23 per cent.; calculated, 25·70 per cent.)

The *calcium salt* separates slowly in the form of feathery groups of needles when solutions of calcium acetate and sodium tartrarsenite are mixed, but it is so unstable in presence of water that it breaks up almost at once into calcium tartrate and arsenious oxide.

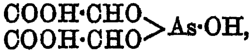
Sodium tartrarsenite gives precipitates with solutions of salts of the heavy metals, but these appear to be in most cases mixtures of a tartrate with arsenious oxide.

According to Clarke and Stallo (*Amer. Chem. J.*, 2, 319), tartar emetic is the potassium salt of an unstable tartrantimonious acid, $OH\cdot Sb\!:\!C_4H_4O_6$, which must be regarded as a derivative of orthantimonious acid, $Sb(OH)_3$, because, when heated with water, it is decomposed into this substance and tartaric acid. It therefore appeared probable that the compounds described above should similarly be regarded as salts of a *tartrarsenious acid*, $OH\cdot As\!:\!C_4H_4O_6$, which would thus be represented as a derivative of the hypothetical ortharsenious acid, $As(OH)_3$. Several attempts were made to prepare tartrarsenious acid, but hitherto it has not been possible to isolate it on account of its instability, although strong evidence of its existence in aqueous solution has been obtained.

As all the tartrarsenites are decomposed when treated with mineral acids in excess, arsenious oxide being precipitated, it is necessary, in order to obtain free tartrarsenious acid, that the decomposition of its salts should be carried out in such a way as to avoid the least excess of the mineral acid. The following method was finally adopted. The barium salt, reduced to fine powder, was suspended in about ten times its weight of water, and rather less than the quantity of dilute sulphuric acid necessary for its complete decomposition was added very gradually and with constant stirring. After some time, the precipitated barium sulphate was filtered off, and a clear solution was obtained which remained unaltered even after standing for several weeks, and was not affected by dilution with four or five times its volume of water. The solution was strongly acid, but contained no sulphuric acid, and when hydrogen sulphide was passed through it a copious precipitate of arsenious sulphide was thrown down, though only a trace of barium tartrarsenite was present in it. There seemed to be no doubt, therefore, that the solution contained tartrarsenious acid, but, as already stated, all attempts to isolate the acid failed. When a portion of the solution was concentrated on the water bath, arsenious oxide was deposited and tartaric acid was left in solution, and the same change occurred when another portion was left to evaporate spontaneously over sulphuric acid. A third portion was mixed with an equal volume of alcohol, but after standing for two days it decomposed in the same way, whilst another portion underwent decomposition when heated to a temperature of 60—70°. The addition of a drop or two of sulphuric or other mineral acid to the solution caused immediate decomposition, and consequent precipitation of arsenious oxide; hence the necessity for avoiding excess of sulphuric acid in the preparation of tartrarsenious acid. The solution decomposed sodium carbonate with effervescence, and as soon as the neutral point was reached arsenious oxide began to separate, whilst disodium tartrate was formed. To a portion of the solution, half the quantity of sodium carbonate required for neutralisation was added, and the solution thus obtained was divided into two parts; on evaporating one part, crystals of sodium tartrarsenite were obtained, and the addition of barium chloride to the other part caused the precipitation of the characteristic barium salt. From these experiments, it may be concluded that tartrarsenious acid, $OHAsC_4H_4O_6$, can exist in aqueous solution, and that, if the solution is not too concentrated, it is stable at the ordinary temperature. In confirmation of this view, the following quantitative experiment was made. A quantity of barium tartrarsenite weighing 6·33 grams was decomposed in the manner already described by 2·40 grams of sulphuric acid. The precipitate was well washed, the filtrate and washings were made up to 100 c.c., and the arsenic estimated in aliquot parts of this solution, with the result that it was found to contain altogether 1·30 grams of arsenic. Now the quantity of sulphuric acid used was sufficient to decompose 5·426 grams of the barium salt, which should yield 4·11 grams of tartrarsenious acid containing 1·29 grams of arsenic. The agreement between theory and experiment is so close as to justify the conclusion that the solution contained a definite compound.

As regards the constitution of the tartrarsenites, it is not yet possible to arrive at a definite conclusion, but it is at least almost certain that they are not double tartrates containing a basic (AsO) radicle in place of a metal. We have found that salts of other hydroxy-acids interact with arsenious oxide in a similar way to the primary tartrates, and yield compounds which are now under investigation, and further that it is hydroxy-acids alone which are capable of behaving in this way. Thus, for example, if arsenious oxide is boiled with solutions of primary oxalates or succinates of sodium or potassium, no double salt is formed, and nothing occurs except dissolution of some of the arsenious oxide in the water present. Again, the formation of the alkali tartrarsenites resembles the formation of ethereal salts rather than the production of a simple salt, for it proceeds slowly and reaches limits depending on the concentration of the solutions and on the relative masses of arsenious oxide and tartrate, and the tartrarsenites appear to be all more or less easily decomposed by the continued action of water. It must be added that this view of the constitution of tartrarsenites is supported by the experiments of Adam (*loc. cit.*) with certain hydroxy-acids and such acidic oxides as boric oxide.

It is to be inferred, then, that arsenious oxide enters into action with one or both of the alcoholic hydroxyl groups and not with the carboxylic hydroxyl of a primary tartrate, and, if this be admitted, two formulæ are possible for tartrarsenious acid, namely, (1)



$$\left.\begin{array}{l}\mathrm{COOH{\cdot}CHO}\\ \mathrm{COOH{\cdot}CHO}\end{array}\right>\mathrm{As{\cdot}OH},$$

according to which it is a derivative of arsenious acid, and (2) $COOH{\cdot}CHO(AsO){\cdot}CH(OH){\cdot}COOH$, in which it is represented as an ethereal derivative of tartaric acid. In order to ascertain the basicity of the acid, we endeavoured to prepare di- and tri-metallic salts, the possible existence of which is indicated by these formulæ, but it was found that the primary salts alone are sufficiently stable to be isolated. A solution of the sodium salt, as stated above, has a strongly acid reaction (the other salts have the same property), and on experiment it was found that exactly 1 mol. NaOH was required to neutralise a solution containing 1 mol. $AsO{\cdot}NaC_4H_4O_6$. Almost at once, however, the disodium salt, which presumably is then formed, breaks up into arsenious oxide and disodium tartrate. Experiments at present in progress with other hydroxy-acids appear to support the first of the formulæ given above, but the evidence as yet is not decisive.

It was to be expected that arsenic acid, also, would form derivatives corresponding to the tartrarsenites, and to test the matter we prepared the potassium and sodium salts of what may be regarded as *tartrarsenic acid.* These compounds were obtained by dissolving the primary tartrates of potassium and sodium in hot solutions of arsenic acid, more than the calculated quantity of the latter being used. In each case dissolution took place readily, and after heating for some time the addition of alcohol threw down white, finely-crystalline precipitates. The salts are, however, unstable in aqueous solution, except in presence of arsenic acid, so that it is difficult to get them sufficiently pure for analysis; at the same time, there seems little doubt that they are "tartrarsenates," of the formulæ $AsO_2M'C_4H_4O_6 + xH_2O$. A fuller investigation of these and other salts is now being carried on.

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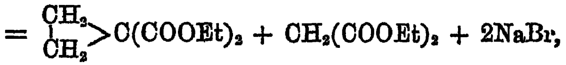
XV.—*The Condensation of Ethylic Trimethylenedicarboxylate with Ethylic Malonate.*

By W. A. BONE, Ph.D., and W. H. PERKIN, jun.

WHEN the sodium derivative of ethylic malonate is digested in alcoholic solution with ethylene bromide, the principal product of the action is ethylic trimethylenedicarboxylate (Trans., 1885, **47**, 807),

$$2CHNa(COOEt)_2 + CH_2Br{\cdot}CH_2Br$$

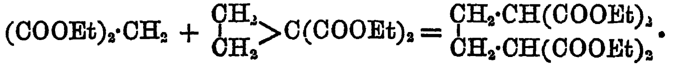


$$= \begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix}\!\!>C(COOEt)_2 + CH_2(COOEt)_2 + 2NaBr,$$

but at the same time, ethylic butanetetracarboxylate is formed in small quantity,

$$2(COOEt)_2CHNa + BrCH_2{\cdot}CH_2Br$$
$$= (COOEt)_2CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH(COOEt)_2 + 2NaBr.$$

Although the amount of this ethereal salt, thus obtained, is always very small, seldom being more than 3 per cent. of the theoretical, it is so valuable for synthetical work that numerous experiments were made, with the object of improving the yield, and ultimately a satisfactory method was devised, which is described in detail in a paper published a short time since (Trans., 1894, **65**, 578). It was there shown that, if ethylene chloride be used instead of ethylene bromide, a distinct increase in the yield of ethylic butanetetracarboxylate is obtained; but the principal product in this case also appears to be ethylic trimethylenedicarboxylate, much ethylic malonate being recovered unchanged. If, now, the mixture of the two substances, thus recovered, be again heated with sodium ethoxide and ethylene chloride, as described in detail in the paper referred to, the yield of ethylic butanetetracarboxylate is enormously increased, amounting, as it frequently does, to 50 per cent. of the product.* The reason for this remarkable increase has now been ascertained, and it has been found that the addition of ethylene chloride in the second instance is unnecessary; for when ethylic trimethylenedicarboxylate and ethylic malonate are heated with sodium ethoxide, they react readily, forming ethylic butanetetracarboxylate.



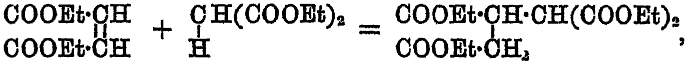
$$(COOEt)_2\cdot CH_2 + \begin{array}{l}CH_2\\ |\\ CH_2\end{array}\!\!>C(COOEt)_2 = \begin{array}{l}CH_2\cdot CH(COOEt)_2\\ |\\ CH_2\cdot CH(COOEt)_2\end{array}.$$

That the product really has this constitution is readily proved by hydrolysing it with alcoholic potash and subsequently heating the butanetetracarboxylic acid at 200°, when adipic acid is quantitatively formed, thus.

$$(COOH)_2CH\cdot CH_2\cdot CH_2\cdot CH(COOH)_2 = COOH\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot COOH + 2CO_2.$$

It is a well-known fact that the ethereal salts of unsaturated acids, in which the double or treble linking is situated between two carbon atoms, one of which is directly united to the carboxyl group, readily act on ethylic malonate in the presence of sodium ethoxide, with formation of condensation products (Michael, *J. pr. Chem.*, **35**, [2], 349; Auwers, *Ber.*, 1891, **24**, 307, 1923, 2887; and others).

A mixture of ethylic fumarate and ethylic malonate, for example, when heated with sodium ethoxide, yield ethylic propanetetracarboxylate,†



$$\begin{array}{l}COOEt\cdot CH\\ \quad\ \ \|\\ COOEt\cdot CH\end{array} + \begin{array}{l}CH(COOEt)_2\\ |\\ H\end{array} = \begin{array}{l}COOEt\cdot CH\cdot CH(COOEt)_2\\ \quad\ \ |\\ COOEt\cdot CH_2\end{array},$$

and this action appears to be general, and shown by all $\alpha\beta$-unsaturated acids, but not by those which, like allylacetic acid,

$$CH_2:CH\cdot CH_2\cdot CH_2\cdot COOH,$$

contain the double linking in any other position.

Obviously, then, in condensing with ethylic malonate to form ethylic butanetetracarboxylate, ethylic trimethylenedicarboxylate behaves exactly as if it were the ethereal salt of an $\alpha\beta$-unsaturated acid, and this remarkable condensation is very interesting in view of its bearing on the constitution of ethylic trimethylenedicarboxylate.

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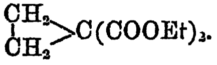
* In the description of this process (*loc. cit.*, p. 579, line 9), instead of "four bottles," read "eight bottles."

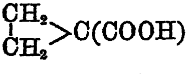
† In all these actions, for the sake of simplicity, the intermediate formation of the sodium derivatives of the ethereal salts has not been represented.

As representing the constitution of this product of the action of ethylene bromide on ethylic malonate, two formulæ have been proposed, namely.

I.  $\begin{matrix}CH_2\\ | \\ CH_2\end{matrix}\!>C(COOEt)_2$. *Ethylic trimethylenedicarboxylate*, Perkin (Trans., 1885, **47**, 817).

II. $CH_2{:}CH{\cdot}CH(COOEt)_2$. *Ethylic vinylmalonate*, Fittig (*Annalen*, 1885, **227**, 25).

The dibasic acid derived from this ethereal salt, on hydrolysis, must, therefore, be either trimethylenedicarboxylic acid,

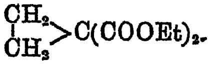


$$\begin{matrix}CH_2\\ | \\ CH_2\end{matrix}\!>C(COOH)_2 \text{ (I)},$$

or vinylmalonic acid, $CH_2{:}CH{\cdot}CH(COOH)_2$ (II).

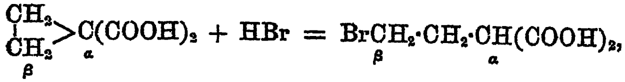
As the result of a long series of investigations, it has been clearly proved that these substances are trimethylene derivatives, and not unsaturated compounds, and this view is now generally adopted (see *Beilstein's Handbuch*, Band I, 711, and Victor Meyer und Paul Jacobson, *Lehrbuch der Organischen Chemie*, Band II, 18).

No doubt, in many respects, these and other trimethylene derivatives behave like unsaturated compounds,* forming additive compounds with bromine, hydrogen bromide, sulphuric acid, &c., whilst, on the other hand, they exhibit properties which preclude the possibility of their being ordinary unsaturated compounds, and, in fact, their whole behaviour is in complete harmony with their constitution as trimethylene derivatives, as Baeyer has indicated in his "Spannung's Theorie" (*Ber.*, 1885, **18**, 2277; compare Trans., 1894, 951). The formation of ethylic butanetetracarboxylate from ethylic malonate and ethylic trimethylenedicarboxylate, as described above, is a further proof of the correctness of this view, and can only be explained on the assumption that the latter ethereal salt has the constitution



$$\begin{matrix}CH_2\\ | \\ CH_3\end{matrix}\!>C(COOEt)_2.$$

When trimethylenedicarboxylic acid yields additive products, it behaves exactly as if it were an *αβ*-unsaturated acid; for example, with hydrogen bromide it yields *ω*-bromethylmalonic acid,



$$\begin{matrix}CH_2\\ | \\ \underset{\beta}{CH_2}\end{matrix}\!>\underset{\alpha}{C}(COOH)_2 + HBr = Br\underset{\beta}{C}H_2{\cdot}CH_2{\cdot}\underset{\alpha}{C}H(COOH)_2,$$

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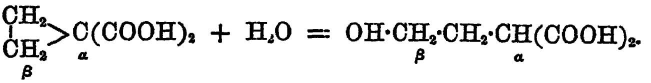
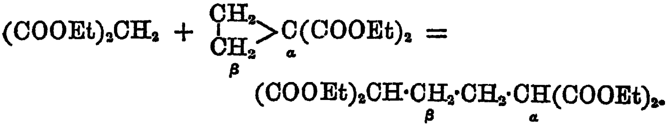
* It is the intention of one of us, on a future occasion, to give a short summary of the methods of formation and of the properties of trimethylene compounds, in order, if possible, to show clearly the points of similarity and difference between these compounds and unsaturated substances.

and, when warmed with dilute sulphuric acid, it is converted into carbobutyrolactonic acid,



$$\underset{\beta}{\begin{array}{l}CH_2\\|\\CH_2\end{array}}\!>\underset{\alpha}{C}(COOH)_2 + H_2O = OH\cdot CH_2\cdot\underset{\beta}{CH_2}\cdot\underset{\alpha}{CH}(COOH)_2.$$

So also in the present instance, when ethylic trimethylenedicarboxylate combines with ethylic malonate to form ethylic butanetetracarboxylate, it behaves like the ethereal salt of an $\alpha\beta$-unsaturated acid, and, on this assumption, the action becomes perfectly clear, and is represented in its simplest form, thus.

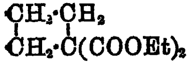


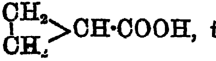
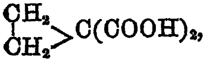
$$(COOEt)_2CH_2 + \underset{\beta}{\begin{array}{l}CH_2\\|\\CH_2\end{array}}\!>\underset{\alpha}{C}(COOEt)_2 =$$
$$(COOEt)_2CH\cdot CH_2\cdot\underset{\beta}{CH_2}\cdot\underset{\alpha}{CH}(COOEt)_2.$$

Similarly, when the sodium derivative of ethylic methylmalonate is employed, ethylic methylbutanetetracarboxylate,

$$(COOEt)_2CMe\cdot CH_2\cdot CH_2\cdot CH(COOEt)_2,$$

is formed, and other trimethylenecarboxylic derivatives appear to behave in like manner, clearly showing that they are not $\beta\gamma$-unsaturated compounds, as suggested by Fittig.

It is interesting to note here that condensation does not take place when a mixture of ethylic tetramethylenedicarboxylate,  $\begin{array}{l}CH_2\cdot CH_2\\ |\quad\;\;\; |\\ CH_2\cdot C(COOEt)_2\end{array}$ and ethylic malonate is heated with sodium ethylate.

Included in this paper is an account of the physical properties of trimethylenecarboxylic acid,  $\begin{array}{l}CH_2\\|\\CH_2\end{array}\!>CH\cdot COOH$, the determination of which, as well as the further study of the chemical properties of the substance, show clearly its relationship to the dicarboxylic acid,  $\begin{array}{l}CH_2\\|\\CH_2\end{array}\!>C(COOH)_2$, from which it is prepared, and support the view that it is a derivative of trimethylene, and not an unsaturated compound.

We are engaged on a further study of the behaviour of trimethylene derivatives towards ethylic malonate, ethylic acetoacetate, and other allied compounds.

Condensation of Ethylic 1 : 1-*Trimethylenedicarboxylate with Ethylic Malonate.*

The ethylic trimethylenedicarboxylate required for these experiments was prepared by heating the sodium derivative of ethylic malonate with ethylene dibromide in alcoholic solution under pressure for 8—10 hours at 100°; the details of the process are similar to those already given (Trans., 1885, **47**, 808), about 350 grams of ethylic malonate being used. The product, after being extracted with ether in the usual way, was very carefully fractionated at ordinary pressure, and about 240 grams, distilling over between 180° and 225°, collected. This fraction was mixed with a solution of 17 grams of sodium in absolute alcohol and 72 grams of ethylene dibromide, and the mixture heated in three soda-water bottles at 100° for five hours; the product, isolated and extracted in the usual manner, was submitted to a careful fractionation under the ordinary pressure. About 195 grams distilled between 180° and 225°, of which at least two-thirds came over above 200°. Of this fraction, approximately one-third was considered to consist of unchanged ethylic malonate and two-thirds of ethylic trimethylenedicarboxylate (b. p. 208°).

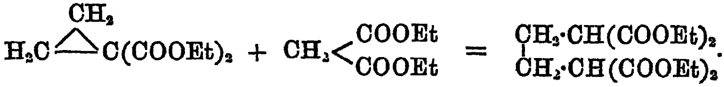
Fifty grams of this product were now mixed with 30 grams of ethylic malonate, the mixture added to a solution of 7 grams of sodium dissolved in 90 grams of absolute alcohol, and this solution of ethylic trimethylenedicarboxylate with the sodium derivative of ethylic malonate heated in soda-water bottles at 100° for eight hours. As much as possible of the alcohol having been distilled off, the dark red residue was mixed with water and acidified with dilute hydrochloric acid; the thick, reddish oil which separated was extracted with ether, and the ethereal solution, after being well washed with water and dilute sodium carbonate solution, was dried over calcium chloride, and the ether distilled off. The residual red oil was now fractionated under reduced pressure (40 mm.), when about a quarter of the whole passed over below 180°, and was found, on examination, to consist of a mixture of ethylic 1 : 1-trimethylenedicarboxylate and ethylic malonate. The temperature then rose rapidly, and from 60 to 70 grams passed over between 210° and 240°. A small quantity of this oil, collected at 238—240° (40 mm.), gave the following results on analysis, showing it to consist of ethylic butanetetracarboxylate.

	Found.	Theory. $C_{16}H_{26}O_8$.
C	55·21 per cent.	55·49 per cent.
H	7·60 „	7·51 „

Hydrolysis of the Oil.—In order to prove that this oil was ethylic butanetetracarboxylate, it was mixed with three times its volume of concentrated hydrochloric acid, glacial acetic acid added until the oil just dissolved, and the whole digested several hours in a reflux apparatus on a sand bath; steam was then driven through the liquid until the whole of the acetic acid had been removed, and the solution filtered and evaporated to a small bulk on the water bath. After a time, crystals formed; these were separated from the mother liquor, redissolved in water, and the aqueous solution boiled with animal charcoal; the solution was then filtered and concentrated until crystallisation commenced. On standing, colourless crystals were deposited, which melted at 149°, and resembled adipic acid in all respects. Analysis.

	Found.	Theory. $C_6H_{10}O_4$.
C	49·01 per cent.	49·31 per cent.
H	6 87 ,,	6·85 ,,

This formation of adipic acid proves conclusively that ethylic butanetetracarboxylate had been formed by the condensation of ethylic trimethylenedicarboxylate with ethylic malonate, thus.



We have also prepared ethylic butanetetracarboxylate from the low boiling product of the action of ethylene dichloride on the sodium derivative of ethylic malonate (Trans., 1894, **65**, 579). For this purpose, 94 grams of the product which, after a second fractionation, distilled over between 200° and 230° (under ordinary atmospheric pressure), was mixed with a solution of 6·5 grams of sodium in 80 grams of absolute alcohol, and heated for nine hours at 100° in a soda-water bottle. It was then poured into water, the solution acidified with dilute hydrochloric acid, and the heavy oil which separated extracted with ether; the ethereal solution, after being washed with a dilute solution of sodium carbonate and with water, was dried over calcium chloride, and the ether distilled off. The oily residue was first distilled under the ordinary pressure, when 30 grams came over below 230°; the distillation was then continued under reduced pressure (70 mm.), when the oil began to pass over at 180°, and two fractions were collected, one at 180—225°, and the other at 225—240°.

This higher fraction (225—240°), when hydrolysed by means of a mixture of concentrated hydrochloric and glacial acetic acids in the manner already described, yielded colourless crystals melting at 149·5°, and possessing all the properties of adipic acid.

Analysis of the acid gave the following numbers.

	Found.	Calculated for adipic acid.
Carbon	48·84 per cent.	49·31 per cent.
Hydrogen	6·73 ,,	6·85 ,,

Condensation of Ethylic Trimethylenedicarboxylate with Ethylic Methylmalonate. Formation of Ethylic Methylbutanetetracarboxylate, $(COOEt)_2CMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH(COOEt)_2$.

In order to bring further evidence in support of this remarkable property of ethylic trimethylenedicarboxylate, experiments were tried with the object of obtaining a condensation product from this compound and ethylic methylmalonate. In doing this, it was found to be unnecessary to isolate the ethylic trimethylenedicarboxylate, provided all the ethylic malonate in the mixture of this substance with ethylic trimethylenedicarboxylate (p. 112) was converted into the mono- or di-methyl derivative. To effect this, 180 grams of the mixture was added to a solution of 12·6 grams of sodium in 160 grams of ethylic alcohol, then 80 grams of methylic iodide, and the whole heated on the water bath in a reflux apparatus for one hour; in this way, the ethylic malonate present was completely transformed into the mono- or di-methyl derivative, the large quantity of sodium ethylate and methylic iodide employed ensuring the complete conversion of the ethylic malonate. After the excess of alcohol had been distilled off on the water bath, the product was poured into water, and the oil which separated was extracted with ether. The ethereal solution, after being well washed with a dilute solution of sodium thiosulphate, to remove iodine, and then with water, was dried over calcium chloride, and the ether distilled off; the oily residue, on fractionation, yielded a colourless oil distilling between 180° and 220°. 90 grams of this oil was mixed with 40 grams of ethylic methylmalonate, the whole added to 12 grams of sodium dissolved in 150 grams of absolute alcohol, and the mixture heated in soda-water bottles for 10 hours at 100°. After distilling off as much alcohol as possible on the water bath, the product was poured into water, acidified with dilute hydrochloric acid, and extracted with ether. The ethereal solution, after being well washed with dilute sodium carbonate solution and with water, was dried over calcium chloride, and the ether distilled off. The residual oil, when distilled under reduced pressure (40 mm.), gave 60 grams of distillate below 180°; the thermometer then rose rapidly, and 25 grams came over between 200° and 250°; the greater portion of this, when refractionated, passed over at 240° (40 mm.), and was analysed with the following results.

	Found.	Calculated for $C_{17}H_{28}O_8$.
Carbon	56·09 per cent.	56·66 per cent.
Hydrogen	7·81 „	7·77 „

The oil is therefore ethylic methylbutanetetracarboxylate, and its constitution is proved by the fact that, on hydrolysis and subsequent distillation, it yields α-methyladipic acid,

$$COOH{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}COOH.$$

α-Methyladipic acid.

Hydrolysis of the Oil.—Twenty-five grams of the oily ethylic methylbutanetetracarboxylate just described were carefully added to a well-cooled solution of 25 grams of potassium hydroxide in methylic alcohol. Very little action took place in the cold, but on heating in a reflux apparatus on the water bath, the potassium salt of the acid separated in minute crystals. After heating for eight hours, the product was poured into water, the liquid evaporated until free from methylic alcohol, and the solution, which should be as concentrated as possible, was acidified with hydrochloric acid, and extracted several times with pure ether. The ethereal solution, after being dried over calcium chloride and evaporated, left a thick, almost colourless syrup, presumably methylbutanetetracarboxylic acid. This, when distilled under reduced pressure (60 mm.), evolved carbon dioxide, a colourless acid distilling over between 250° and 260°; the latter, on being allowed to remain over night, solidified to a white crystalline mass of nearly pure α-methyladipic acid, which was spread out on a porous plate and allowed to stand for some days, until free from oily mother liquor. Great difficulty was experienced in recrystallising this acid, owing to its excessive solubility, and the slight tendency it has to crystallise, in which respect it differs in a marked manner from adipic acid. The most satisfactory results were obtained by dissolving the acid in a very small quantity of water, and evaporating in a vacuum over concentrated sulphuric acid; the thick syrup which was left deposited ill-defined nodular masses when left for a week or more in a vacuum; these were dried, first on a porous plate, then in a vacuum over sulphuric acid, and analysed.

	Found.	Theory. $COOH{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}COOH.$
Carbon........	52·10 per cent.	52·50 per cent.
Hydrogen	7·34 „	7·50 „

α-Methyladipic acid melts at about 64°, but this melting point must be taken as only approximate, owing to the difficulty experienced in recrystallising the acid.

It is excessively soluble in water, readily in alcohol and ether, and sparingly in cold, but readily in hot benzene or light petroleum. If the benzene solution be allowed to evaporate slowly in the air, the acid separates in stellate groups of minute foliated crystals.

Salts of a-Methyladipic acid.

Calcium Salt.—This differs from the corresponding salt of adipic acid in being somewhat readily soluble in water; no precipitate is formed on adding excess of a concentrated solution of calcium chloride to a neutral solution of the ammonium salt of the acid, but on carefully concentrating the mixture on the water bath, the calcium salt separates in colourless needles.

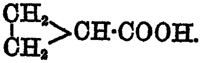
Silver Salt.—On adding a solution of silver nitrate to the neutral solution of the ammonium salt, a white precipitate of the silver salt is formed immediately. It is moderately soluble in hot, but only slightly in cold water. For analyses, the salt was dried, first on a porous plate, and then in a vacuum over sulphuric acid; it may be exposed to diffused daylight for several hours without any change in colour, and may be dried at 100° without any perceptible decomposition.

The salt was analysed in two ways: (I) it was decomposed by dilute nitric acid, and the silver precipitated by dilute hydrochloric acid; (II) it was carefully ignited, and the residual silver weighed.

Calculated for $C_7H_{10}O_4Ag_2$.. Silver = 57·75 per cent.
Found .... „ (I) 57·78; (II) 57·81 per cent.

It seemed interesting and important to ascertain whether this remarkable property of trimethylene compounds of forming additive compounds with ethylic malonate is shared by the corresponding tetramethylene derivatives. We accordingly prepared ethylic 1:1-tetramethylenedicarboxylate by the action of trimethylene bromide on the sodium compound of ethylic malonate, the details of the method have already been given by one of us (Trans., 1887, **51**, 2). This was then mixed with the calculated quantity of ethylic malonate and sodium ethylate, in alcoholic solution, and the whole was heated in a sealed tube for nine hours at 100°. On isolating the product in the usual manner, it was found to consist entirely of ethylic malonate and tetramethylenedicarboxylate. Evidently, then, under these circumstances detailed in this paper, the tetramethylene is much more stable than the trimethylene ring.

Trimethylenecarboxylic acid,



$\overset{CH_2}{\underset{CH_2}{|}}\!>CH\cdot COOH.$

The properties of this important derivative of trimethylene have, so far, not been carefully studied;* and it therefore appeared to us that it would be interesting to prepare as pure a sample as possible of the substance, in order that its physical constants might be determined.

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* The work already done on this acid is contained in the following papers: Fittig and Roeder, *Annalen*, 1885, **227**, 25; W. H. Perkin, jun., *Ber.*, 1884, **17**, **57**; and 1885, **18**, 1738; Trans., 1885, **47**, 815.

For this purpose, 1 : 1-trimethylenedicarboxylic acid was highly purified and submitted to distillation; the distillate, consisting of a mixture of trimethylenecarboxylic acid and butyrolactone, was then dissolved in water, sodium carbonate added until the liquid was alkaline, and the butyrolactone removed by repeated extraction with purified ether. The alkaline solution was next acidified, and the trimethylenecarboxylic acid extracted with pure ether; the ether having been distilled off, the treatment with sodium carbonate was repeated, in order to remove the last traces of butyrolactone, and the acid finally purified by careful fractionation.

The portion boiling at 182—183°—that used in the experiment described below—gave the following results on analysis.

	Found.	Theory. $C_4H_6O_2$.
C	55·57 per cent.	55·81 per cent.
H	7·13 ,,	6·98 ,,

Trimethylenecarboxylic acid is miscible with water in all proportions; the "dissociation constant" was kindly determined by Dr. Walker, who found $\kappa = 0·0014$; but the results were not quite so sharp as could have been wished, owing, possibly, to slight decomposition of the acid in aqueous solution.

The determinations of the density, magnetic rotation, and refractive power of this acid were carried out by W. H. Perkin, sen., with the following results.

Relative Density Determinations.

$d\,4°/4° = 1·1024$. $d\,10°/10° = 1·0966$. $d\,15°/15° = 1·0923$.
$d\,20°/20° = 1·0884$. $d\,25°/25° = 1·0848$.

Magnetic Rotation.

This was twice determined, and the numbers given are the mean of 64 readings.

t.	Sp. rotation.	Mol. rotation.
18·6°	0·9443	4·141

The value estimated as butyric acid minus H_2, assuming the acid to be saturated, is 3·964; on the other hand, an unsaturated acid of this formula would have the calculated value 5·584. α-Crotonic acid, $CH_3·CH⁚CH·COOH$, calculated from the magnetic rotation of its ethylic salt, has the value 5·589. These numbers, therefore, prove clearly that trimethylenecarboxylic acid cannot be an unsaturated acid.

Refractive Power.

Line	μ.	$\frac{\mu-1}{d}$.	$\frac{\mu-1}{d}p$.
A.............	1·43196	0·39649	34·098
H_{α}	1·43500	0·39928	34·338
D	1·43763	0·40170	34·546
H_{β}.............	1·44388	0·40743	35·039
H_{γ}.............	1·44910	0·41222	35·451
H (estimated) ..	—	—	35·800

The *dispersion* H — A is about 1·70.

The formula $C_4H_6O_2$, estimated for A by Gladstone's value, requires, if saturated, 34·00, if unsaturated, 35·10; by Bruhl's value for H_{α}, if saturated, 34·00, but if unsaturated, 36·3. The experimental result thus confirms the constitution deduced from the magnetic rotation determinations, showing that trimethylenecarboxylic acid cannot be an unsaturated compound.

In connection with this point, the behaviour of this acid towards permanganate in alkaline solution is also interesting.

If the pure acid be dissolved in a slight excess of sodium carbonate at 0°, the solution will not decolorise permanganate at once, but does so on long standing, and very rapidly if the solution is gently warmed. The acid is much more stable towards permanganate than an unsaturated acid, but is, on the other hand, much more readily oxidised than the corresponding tetramethylenecarboxylic acid; this is what might be expected, from the study of the chemical properties of the two acids.

Action of Hydrogen Bromide on Trimethylenecarboxylic acid. Formation of γ-Bromobutyric acid, $CH_2Br{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$.

Trimethylenecarboxylic acid dissolves readily in fuming hydrobromic acid with slight development of heat, and there is apparently little action in the cold; on heating in a sealed tube at 175°, however, decomposition takes place readily, and the contents of the tube separate into two layers. The product was poured into water, the oily layer extracted with ether, and the ethereal solution well washed with water and dried over calcium chloride; on evaporating, an almost colourless oil was obtained, which solidified to a mass of crystals on cooling; these, after standing over sulphuric acid in a vacuum, in contact with porous porcelain, became colourless, and, on analysis, gave the following results.

	Found.	Theory. $C_4H_7BrO_2$.
Br	48·32 per cent.	47·90 per cent.

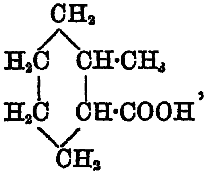
This substance melts at 33—35°, and is obviously identical with the γ-bromobutyric acid, melting at 32—33°, obtained by Henry (*Bull. Soc. Chim.*, **46**, 65) from γ-butyrolactone, by the action of hydrobromic acid.

This experiment shows that trimethylenedicarboxylic acid and trimethylenemonocarboxylic acid behave similarly when treated with hydrobromic acid, both yielding γ-bromo-additive products.

Owens College Chemical Laboratory,
Manchester.

XVI.—cis- *and* trans-*Hexahydro-orthotoluic Acids.*

By W. Goodwin and W. H. Perkin, jun.

Some time since, one of us, in conjunction with P. C. Freer (Trans., 1888, **53**, 208), prepared a methylhexamethylenecarboxylic acid (hexahydro-orthotoluic acid),  $$CH_2\langle\begin{matrix}CH_2\cdot CH_2\cdot CH\cdot CH_3\\ CH_2\cdot CH\cdot COOH\end{matrix}$$, from the product of the action of methylpentamethylene dibromide,

$$CH_3\cdot CHBr\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2Br,$$

on the sodium derivative of ethylic malonate, and described it as a colourless oil boiling at 235—236°.

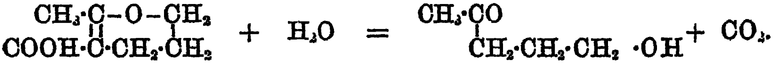
Recently Markownikoff (*J. pr. Chem.*, 1894, **49**, 65) has studied the reduction products of orthotoluic acid, obtained by treating a boiling solution of the acid in amylic alcohol with a large excess of sodium, and has isolated a hexahydro-orthotoluic acid, which boils at 240°, and solidifies readily on cooling, the pure acid melting at 50—52°; no mention whatever is made of the work of Perkin and Freer, the author being apparently ignorant of its existence.

The wide difference in properties between the synthetical acid and the acid obtained by reduction made it desirable that the whole subject should be reinvestigated, with a view of determining whether these acids are in reality isomeric, and if so, what the nature of the isomerism is; with this object in view, we, in the first place, prepared Markownikoff's acid, following this author's directions as closely as possible.

As the result of a careful examination of this acid, we are able to confirm his description of its properties in every particular. Perhaps the most important property, in view of the present question of isomerism, is the ease with which the acid solidifies after distillation, even when not quite pure. We prepared also the anilide of the acid, $C_7H_{13}\cdot CO\cdot NH\cdot C_6H_5$, which has not hitherto been described, in order to compare it with the anilide of the synthetical acid; it crystallises beautifully from light petroleum, and melts at 148°.

In discussing the question of the isomerism of these two acids, it will be necessary to show, in the first place, that the acid described by Freer and Perkin is a hexahydro-orthotoluic acid, and therefore *structurally identical* with Markownikoff's acid, and, in order to do this, it will be well to give briefly the method by which it was synthesised.

The starting point in the synthesis is acetobutylic alcohol. This is prepared by digesting methyldehydrohexonecarboxylic acid with water as long as carbon dioxide is evolved (Trans., 1889, **51**, 718), when the following decomposition takes place.



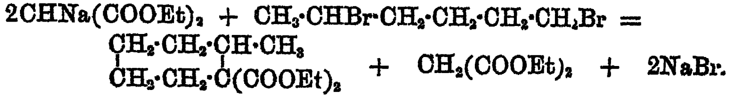
$$\begin{array}{l} CH_3\cdot C-O-CH_2 \\ COOH\cdot C\cdot CH_2\cdot CH_2 \end{array} + H_2O = \begin{array}{l} CH_3\cdot CO \\ CH_2\cdot CH_2\cdot CH_2\cdot OH \end{array} + CO_2.$$

That the ketonic alcohol obtained is, in reality, acetobutylic alcohol, is proved by its behaviour on oxidation; chromic acid converting it, in the first place, into acetobutyric acid, $CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2\cdot COOH$, which, on further oxidation, yields acetic and succinic acids (*loc. cit.*, p. 719).

Acetobutylic alcohol is readily reduced by sodium amalgam, forming δ-hexylene glycol $CH_3\cdot CH(OH)\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH$, from which, by the action of fuming hydrobromic acid, δ-hexylene dibromide is obtained; the latter, judging from the manner in which it is formed, evidently must be represented by the formula

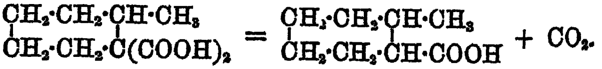
$$CH_3\cdot CHBr\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2Br.$$

If, now, the sodium derivative of ethylic malonate be digested with this dibromide, an action will take place readily, ethylic methylhexamethylene dicarboxylate being produced thus



$$2CHNa(COOEt)_2 + CH_3\cdot CHBr\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2Br =$$
$$\begin{array}{l} CH_2\cdot CH_2\cdot CH\cdot CH_3 \\ CH_2\cdot CH_2\cdot C(COOEt)_2 \end{array} + CH_2(COOEt)_2 + 2NaBr.$$

This ethereal salt, on hydrolysis, yields the corresponding dibasic acid, which, when distilled, is decomposed with formation of methylhexamethylenecarboxylic acid or hexahydro-orthotoluic acid.



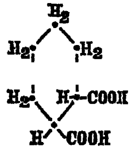
$$\begin{array}{l} CH_2\cdot CH_2\cdot CH\cdot CH_3 \\ CH_2\cdot CH_2\cdot C(COOH)_2 \end{array} = \begin{array}{l} CH_2\cdot CH_2\cdot CH\cdot CH_3 \\ CH_2\cdot CH_2\cdot CH\cdot COOH \end{array} + CO_2.$$

If this synthesis be carefully considered, it is difficult to see how the acid obtained can possibly have any other constitution than that of a hexahydro-orthotoluic acid; unless, indeed, it be an unsaturated acid. This alternative has already been discussed (Trans., 1888, **53**, 208), and it was shown that the magnetic rotation of the acid clearly proves that it cannot be unsaturated; this has since been confirmed by the discovery that the sodium salt of the acid does not decolorise potassium permanganate (Baeyer, *Annalen*, 1888, **245**, 148).

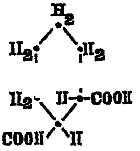
The anilide of the synthetical acid, $C_7H_{13}CO{\cdot}NH{\cdot}C_6H_5$, melts at 66—68°, and differs in its properties widely from the anilide obtained by Markownikoff, which, as already stated, melts at 148°.

From the above statement it must be assumed that the synthetical acid and Markownikoff's hexahydro-orthotoluic acid are structurally identical; obviously then the cause of the well-marked isomerism must be sought in other than purely chemical reasons.

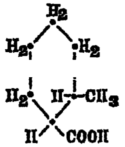
A careful examination of the formula of hexahydro-orthotoluic acid indicates at once that this acid, like hexahydrophthalic acid, may exist in two stereoisomeric modifications



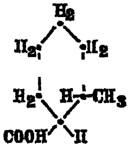
cis-Hexahydrophthalic acid.



trans-Hexahydrophthalic acid.



cis-Hexahydro-orthotoluic acid.



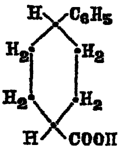
trans-Hexahydro-orthotoluic acid.

The two modifications of hexahydrophthalic acid (Baeyer, *Annalen*, 1890, **258**, 169) are well defined, and it is improbable that the substitution of a methyl or other alkyl group for one carboxyl group in this acid would greatly affect the conditions of isomerism, because crotonic acid, $CH_3{\cdot}CH{:}CH{\cdot}COOH$, and cinnamic acid,

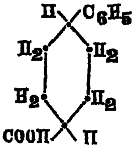
$$C_6H_5{\cdot}CH{:}CH{\cdot}COOH,$$

which are derived from fumaric acid in this way, exist in stereoisomeric forms.

In connection with this point, it is interesting to note that Baeyer and Rassow (*Annalen*, 1894, **282**, 139) have lately shown that paraphenylhexahydrobenzoic acid, like hexahydroterephthalic acid, exists in two well-defined stereoisomeric modifications which melt at 111—113° and 202° respectively.



cis-p-Phenylhexahydrobenzoic acid.



trans-p-Phenylhexahydrobenzoic acid.

These acids are partially convertible into one another by heating with hydrochloric acid; in any case, whether the acid of high melting point or of low melting point is used in the experiment, a condition of equilibrium results, when the product contains 90 per cent. of the former and 10 per cent. of the latter.

In order to show, if possible, that the difference in properties between the two hexahydrotoluic acids was due to stereoisomerism, each was heated with hydrochloric acid at 200°, but without any apparent change, as the solid acid after this treatment and subsequent refractionation again solidified almost completely, and the liquid acid after similar treatment, even when allowed to remain for some time at −10° in contact with a crystal of the solid acid, showed no signs of crystallisation. The same result was always obtained whenever the acids were heated, either with hydrochloric acid or with quinoline, at various temperatures and under various conditions.

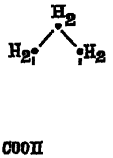
Ultimately it was found that the solid acid, although crystallising with such facility when pure, if mixed with small quantities of the liquid acid, does not solidify at all at −10°, and therefore if, in the above experiments, a partial change of the one isomeride into the other had taken place, the detection of the change by freezing experiments would scarcely be possible; the conversion of the liquid acid into the solid acid was ultimately proved to have taken place in the following manner. A small quantity of the liquid acid which had been twice heated with hydrochloric acid at 200°, and subsequently boiled with quinoline for two days, was converted into the acid chloride by means of phosphorus pentachloride, and from this the anilide was prepared. The crystalline product showed no definite melting point, but on repeated treatment with small quantities of cold ether, the melting point gradually rose until ultimately the residual colourless substance melted at 143—145°, and consisted of the nearly pure anilide of the solid acid, which, as stated above, melts at 148°.

This anilide was now decomposed by heating with hydrochloric acid, and the regenerated acid distilled; on cooling, the distillate at once solidified, in the manner characteristic of the solid acid, and, after purification, the crystals melted at 47—49° instead of at 50—52°.

It is clear, then, that hexahydro-orthotoluic acid exists in two stereoisomeric forms, and that the liquid modification obtained by synthesis, when treated as described above, is converted into the solid modification obtained by Markownikoff by the reduction of orthotoluic acid. It is of course not possible to be certain which of the agents used actually brought about the change; in all probability it was due to the action of the hydrochloric acid, but this is a matter of small importance.

There is some reason for believing that the solid acid also is, to a small extent, converted into the liquid acid by treatment with hydrochloric acid, as the product after fractionation melts below 30°, due to the crystals containing a small quantity of an oily substance, which is readily removed in contact with porous porcelain; the quantity converted, however, is certainly very small. As the solid acid is much more stable towards hydrochloric acid than the liquid acid, it is probably the *trans*-modification, the latter being the *cis*-modification; and this method of distinguishing the isomerides has been adopted in the following pages.

trans-Hexahydro-orthotoluic acid.



Markownikoff (*J. pr. Chem.*, 1894, **49**, 65) prepared this acid by reducing orthotoluic acid in boiling amylic alcohol solution with excess of sodium. As considerable quantities of this acid were required for the experiments described in this paper, about 100 grams of pure orthotoluic acid were reduced in portions of 25 grams at a time, each quantity being four times treated with sodium and amylic alcohol, the details of the operations being the same as recommended by Markownikoff.

On fractionating the combined products, a considerable quantity passed over below 200°, the thermometer then rose rapidly to 230°, and between this temperature and 245° the whole distilled as a colourless oil, which solidified on standing.

The crystals, after being freed from oily matter by contact with porous porcelain, were purified by treatment with permanganate and recrystallisation from benzene, as recommended by Markownikoff; the colourless, crystalline product melted at 50—52°, and, on analysis, gave the following results.

	Found. I.	Found. II.	Theory. $C_8H_{14}O_2$.
C........	67·55	67·40 per cent.	67·61 per cent.
H........	9·89	9·86 ,,	9·86 ,,

This acid has all the properties ascribed to it by Markownikoff; it boils at 240—241°, and, excepting for the facility with which it crystallises at ordinary temperatures, it resembles closely the *cis*-acid, which boils at 236·5—237°.

Anilide of trans-*hexahydro-orthotoluic acid*, $C_7H_{13}{\cdot}CO{\cdot}NH{\cdot}C_6H_5$.

In order to prepare this substance for comparison with the anilide of the *cis*-acid, the pure *trans*-acid was digested in a reflux apparatus with excess of pure aniline for three days. The product, which contained a quantity of crystals, was dissolved in ether, and the ethereal solution after being washed, first with dilute hydrochloric acid and then with sodium carbonate, was dried over anhydrous potassium carbonate and evaporated; the residue, which rapidly solidified, was spread on a porous plate, and subsequently recrystallised from a mixture of benzene and light petroleum, with the aid of animal charcoal. After repeated recrystallisation, the melting point remained constant at 148° and the following results were obtained on analysis.

	Found.	Theory. $C_{14}H_{19}NO$.
N........	6·59 per cent.	6·45 per cent.

The anilide of *trans*-hexahydro-orthotoluic acid crystallises from a mixture of benzene and light petroleum in glistening plates with a slight, bluish fluorescence, somewhat similar to, but much less pronounced than that of anthracene crystals. It is sparingly soluble in ether and light petroleum, readily in alcohol or benzene, but insoluble in water; when heated in small quantities, it distils without decomposition.

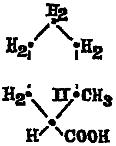
As it appeared possible that, in reducing orthotoluic acid, the *cis*-acid might have been formed along with the *trans*-acid, the liquid products of the action, which are always present in considerable quantity, were carefully investigated; the porous plate, which had been used in the purification of the *trans*-acid, was extracted with ether in a Soxhlet apparatus, and the combined acids submitted to careful fractionation in a Würtz flask fitted with a long neck.

In this way, a disagreeably smelling acid was obtained, which boiled at 176°, and consisted of nearly pure isovaleric acid.

	Found.	Theory. $C_4H_9{\cdot}COOH$.
C........	59·45 per cent.	58·82 per cent.
H........	9·87 ,,	9·80 ,,

This acid is probably produced by the oxidation of the sodium isoamylate formed during the above reduction, and is apparently always present in small quantity in the products of similar reductions, as both Rassow and Markownikoff observed the presence of a disagreeably smelling acid in their products. As soon as the valeric acid had passed over, the temperature rose rapidly to 235°, and the distillate boiling at 235—245° again became almost solid. The oily matter removed from the crystals, as before, on further purification, also solidified, so that apparently the only product of the reduction of orthotoluic acid by sodium and amylic alcohol is *trans*-hexahydro-orthotoluic acid.

cis-*Hexahydro-orthotoluic acid* (*Methylhexamethylenecarboxylic acid*).



The method adopted in preparing this acid was similar to that employed by Freer and Perkin (Trans., 1888, **53**, 206), one or two slight modifications being introduced in purifying the product.

Ethylic methylhexamethylene dicarboxylate was first synthesised by heating methylpentamethylene dibromide (115 grams) with ethylic malonate (160 grams) and sodium ethoxide (23 grams of sodium) in a reflux apparatus for 10 hours. The ethereal salt, isolated in the usual manner, was carefully fractioned, and the portion boiling at 260—265°, and which, as before, contained traces of bromine, hydrolysed by boiling it with twice the calculated quantity of alcoholic potash for five hours. The product, freed from every trace of alcohol by repeated evaporation with water, was cooled, acidified, and extracted three times with ether which had been purified by repeated distillation over sodium; the ethereal solution was then dried over calcium chloride, evaporated, and the oily residue allowed to stand in a cool place for six weeks, over sulphuric acid in a vacuum. At the end of that time, the crystals were collected by means of the pump, freed completely from the thick, oily, mother liquor by contact with porous porcelain, and then recrystallised twice from water. An analysis showed that the crystals were pure methylhexamethylene dicarboxylic acid.

	Found.	Theory. $C_9H_{14}O_4$.
C........	58·10 per cent.	58·06 per cent.
H........	7·68 ,,	7·53 ,,

Methylhexamethylenedicarboxylic acid melts at about 147°, and, although its properties have already been given (*loc. cit*, p. 208), we may here add that the solution of the sodium salt does not decolorise permanganate, thus precluding the possibility of the acid being unsaturated.

In order to obtain the monocarboxylic acid, the pure dibasic acid was distilled, and the oily distillate carefully fractioned; the greater portion boiled at 236·5—237° (the boiling point previously given was 235—236°); but all attempts to obtain this acid in a crystalline condition by leaving it in a freezing mixture in contact with a crystal of the *trans*-acid were fruitless.

On testing the acid with permanganate in alkaline solution, a slight action was noticed; in order, therefore, to still further purify the product, it was dissolved in a dilute solution of sodium carbonate, cooled with ice, excess of permanganate added, and the mixture allowed to stand for half an hour. The permanganate was then destroyed by alcohol, the liquid filtered, evaporated nearly to dryness, and the acid isolated and fractioned as before; it again boiled constantly at 236·5—237°, but, on cooling, showed no signs of crystallising.

On analysis it gave numbers agreeing closely with those required by the formula of hexahydro-orthotoluic acid.

	Found.		
	I.	II.	Theory $C_8H_{14}O_2$.
C........	67·52	67·50 per cent.	67·61 per cent.
H........	9·81	9·92 ,,	9·86 ,,

These analyses were carried out with the products from two distinct preparations.

Anilide of cis-*hexahydro-orthotoluic acid*, $C_7H_{13}\cdot CO\cdot NH\cdot C_6H_5$. —This characteristic derivative was prepared by boiling the purified acid with a considerable excess of aniline for three days in a reflux apparatus; the dark coloured product was dissolved in ether, and after being washed well, first with dilute hydrochloric acid and then with sodium carbonate solution, it was dried over anhydrous potassium carbonate, evaporated, and the residual brownish oil allowed to stand over sulphuric acid in a vacuum until it had completely solidified.

This product differs in its properties in a marked manner from the corresponding anilide of the *trans*-acid, it has little facility for crystallising, and separates from most solvents in the form of an oil. The best way of purifying it is to dissolve the dark coloured, crystalline mass in a large quantity of boiling light petroleum (b. p. 50—60°), and after digesting the solution with purified animal charcoal until the colour becomes pale yellow, to filter and allow the solution to evaporate at the ordinary temperature, when the anilide rapidly separates in long, colourless, silky needles. These crystals were collected, recrystallised from light petroleum, and analysed with the following result.

	Found.	Theory. $C_{14}H_{19}NO$.
N........	6·43 per cent.	6·45 per cent.

The anilide of *cis*-hexahydro-orthotoluic acid melts at 66—68°. It is readily soluble in ether, alcohol, chloroform, and benzene, very sparingly in cold light petroleum, and almost insoluble in water. When rapidly heated in small quantity, it distils apparently without decomposition, yielding an oily distillate, which solidifies only very slowly, even in contact with a crystal of the pure substance.

Conversion of cis-*Hexahydro-orthotoluic acid into* trans-*Hexahydro-orthotoluic acid.*

As explained in the introduction, considerable difficulty was experienced in experimentally proving this isomeric change, owing to the fact that small quantities of the oily *cis*-acid are sufficient to prevent the solid *trans*-acid from crystallising even when the mixture is cooled to −10°.

In the first experiments, the pure *cis*-acid was heated with concentrated hydrochloric acid in a sealed tube for five hours at 190—200°, the slightly brownish product was poured into water, and the oily acid extracted with ether; the ethereal solution was dried over calcium chloride and fractionated, when the whole distilled between 236° and 238° as a colourless oil, which, even at −10°, in contact with a crystal of the *trans*-acid, showed no signs of crystallisation. This same sample was then again heated with hydrochloric acid, but even after this second treatment it did not crystallise. The acid was then boiled with four times its volume of pure quinoline in a reflux apparatus for three days, the product digested with hydrochloric acid, and distilled in a current of steam; the distillate was extracted with ether, and the acid distilled, when again the whole of it passed over between 236° and 238°, but showed no signs of crystallising after standing in contact with a crystal of the *trans*-acid at −10° for half an hour. In order to determine whether any change had taken place, the acid was converted into the acid chloride by treating it with the calculated quantity of phosphorus pentachloride, and the oxychloride removed by passing a current of dry air through the mixture heated at 100° under 50 mm. pressure. The oily residue was then poured into pure aniline, and after the excess of the latter had been removed by shaking the ethereal solution of the product with dilute hydrochloric acid, it was dried over calcium chloride, and evaporated, and the anilide, which, on standing, became nearly solid, was spread on a porous plate and allowed to remain until free from oily mother liquor. As the nearly colourless residue had no definite melting point, it was ground up and extracted repeatedly with small quantities of cold ether; in this way a crystalline product was obtained which melted at 143—145°, and showed all the properties of the anilide of *trans*-hexahydro-orthotoluic acid, melting at 148°.

When this anilide was heated with hydrochloric acid in a sealed tube at 180° for one hour, the contents of the tube extracted with pure ether, the ethereal solution washed with water, dried over calcium chloride, and evaporated, an oily acid was left; this after being freed from ether by passing a current of dry air over it, was distilled and cooled to 0°, when it solidified almost completely. The crystalline mass, left in contact with porous porcelain until free from oil, melted at 41—44°, and after remelting and pressing between blotting paper, the melting point rose to 47—49°; the melting point of *trans*-hexahydro-orthotoluic acid being 50—52°. There can, therefore, be no doubt that during the treatment described above, the liquid *cis*-hexahydroorthotoluic acid had been converted into the stereoisomeric *trans*-modification.

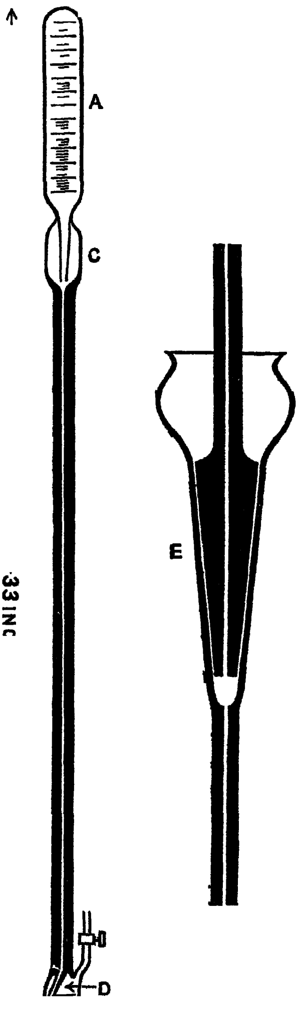
The pure *trans*-acid was treated in exactly the same way as described above in the case of the *cis*-acid, when the product did not solidify until distilled, and even then not completely, as the crystals contained small quantities of an oily impurity readily removed by contact with porous porcelain; possibly this oily substance, which was present only in very small quantity, is the *cis*-acid, but this could not be satisfactorily proved, owing to lack of material.

Owens College Chemical Laboratory,
Manchester.

XVII.—*A New Form of Barometer.*

By J. Norman Collie, Ph.D.

Two years ago I was anxious to make a barometer whose essential features were to be lightness and accuracy. As the instrument would also be subject to a considerable amount of rough usage, since it was needed for other purposes than scientific observations in a laboratory, it also had to be strongly built. It soon appeared that most of the improvements which I was led to embody in this barometer would also be of service in an ordinary laboratory instrument, and, although the original idea is not yet completely worked out, I have made several of the modified barometers, and find that they work well.



In this form of barometer, lightness and also strength are secured by making the stem of narrow-bore tubing, such as is used in the fall tubes of a Sprengel pump. The top, A, and the bottom, B, are made from pieces of the same glass tube, and therefore have necessarily the same bore. At the top of the barometer is a small trap, C, to prevent any air, which may creep up between the mercury and the glass, entering into the top part of the instrument. This idea, I believe, is due to Professor W. Ramsay, who has employed it for many years, and found it work extremely well.

The arrangement for connecting the mercury in the upper part of the barometer with that in the cistern below is, I believe, novel. It consists in fusing a fine capillary tube, D, on to the end of the Sprengel tube, of which the stem of the barometer is made. This capillary is so arranged by bending that it lies close along the inner side of the glass wall of the cistern, B, and dips under the surface of the mercury in the cistern. This serves two purposes; first, it removes out of the way the mercury column connecting the upper part of the barometer with the lower, and allows a good reading to be made in the lower cistern. Secondly, the capillary being of such a fine bore, it is very difficult for air bubbles to penetrate up the barometric stem. Even if such were the case, and some air had entered and risen even half-way up the barometer, by connecting the opening of the lower cistern with a pump, and diminishing the pressure, a current of mercury would descend the Sprengel barometer tube, and the bubbles be thus mechanically carried down in exactly the same manner as they are in an ordinary Sprengel pump, finally rising through the mercury in the lower cistern after they leave the fine capillary tube.

Mr. C. E. Muller has suggested a further improvement, which greatly facilitates filling the barometer. A ground-glass joint, E, is inserted in the middle of the stem. This allows the barometer also to be easily cleaned, and, when not in use, it can be taken apart and put away in a box of not inconvenient length. When thus taken in half, the upper half is, of course, full of mercury, and may be preserved in that condition by slipping a small cap of india-rubber tubing over the end.

Many points could be enumerated showing how convenient is this form of barometer. For instance.

1. It can be easily made by any competent glass-blower.
2. It can be put away in a drawer or elsewhere without any great risk of air entering into the upper cistern, and whether it lies on its side or is upside down makes no difference.
3. There is no difficulty in filling it.
4. It uses a minimum amount of mercury.
5. It is light, strong, and does not easily get out of order.
6. It is extremely accurate.

The graduations may be marked either on the outer wall of the upper and lower cisterns, or on a mirror scale placed behind, which should be made of thick plate glass, in order to avoid parallax. Of course, when great accuracy of reading is required, and there is a ground-glass joint in the stem, the mirror scale only ought to be used, for the objection might be urged that it is impossible to be sure that the junction of the two ground glass surfaces always fitted exactly in the same manner. But there is little doubt that, in practice, this source of error would be exceedingly slight. In reading the height of the barometer which has the graduations on the two cisterns, either a plain mirror may be placed behind the barometer, or a small piece of looking-glass may be held behind by the hand. A convenient method for numbering the scale is to start from the middle as zero, the upper reading is made from below upwards, whilst the lower is from above downwards. The correct height of the barometer is obtained by adding the two readings.

The increase in the height of the meniscus of the mercury when a narrow tube is used in the cisterns is no source of error if the tubes are of equal bore. For the reading in the upper part of the barometer is too high by exactly the same amount as that in the bottom part is too low: the two errors counterbalance one another.

It may be mentioned that I have compared several of these improved barometers with each other, and also with a standard instrument in the physical department of University College, London, with the following results.

Barometers.

	I.	II.	III.	IV.
Diameter of the mercury column at top and bottom of the barometer		$\frac{3}{8}$ inch.	$\frac{7}{8}$ inch.	$\frac{1}{2}$ inch.
Scale.	Brass. mm.	On barometer. mm.	On mirror. mm.	On mirror. mm.
Height on Dec. 17....	762·7	762·8	762·7	762·8
„ „ 18....	748·0	748·1	748·1	748·1
„ „ 19....	747·8	747·6	747·6	747·6
„ „ 20....	760·3	759·8	759·8	759·9

All these readings are corrected for temperature.

I. Standard barometer made by J. Hicks, No. 434, compared with the standard instrument at Kew, December, 1873.

II. Barometer made by J. N. Collie, scale graduated on stem of barometer.

III. Barometer made by Dr. J. Shields and J. N. Collie. Scale graduated on plate-glass mirror by Dr. J. Shields about a year ago.

IV. Barometer made by Mr. C. E. Müller. Scale graduated on plate-glass mirror by J. N. Collie about four years ago.

From these numbers it will be seen that the barometers II, III, and IV give readings which agree amongst themselves, almost within a tenth of a millimetre: an excellent proof, I think, of their accuracy. The only set which are not in agreement with the rest are those of the standard instrument; the maximum difference, however, is only 0·5 mm., by no means a large error.

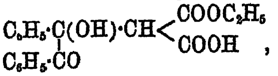
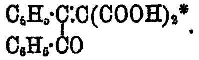
Now, although the scales of II, III, and IV were all made at separate times, they were copied from the same metre steel scale made by Chesterman, of Sheffield, which had been examined some years ago at the Standards Office and found correct. But inasmuch as the parts of the steel scale used were different in each case, and the bore of each of the barometric tubes also varied from three-eighths to seven-eighths of an inch, I think that it will at once be seen that great accuracy may be obtained by the new form of barometer.

One more point might be mentioned which is of importance, namely, the great ease with which this new form of barometer may be obtained free from air. If the boiling be well done, often it is impossible to make the mercury descend in the upper cistern without violent shaking or considerably reducing the pressure on the mercury in the lower cistern.

University College,
London.

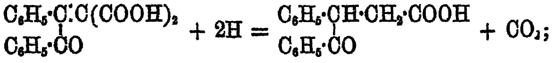
XVIII.—*Condensation of Benzile with Ethylic Malonate.*

By Francis R. Japp, F.R.S., and W. B. Davidson, M.A., B.Sc.

By the condensing action of sodium ethoxide on a mixture of benzile and ethylic malonate we have obtained two compounds: (1) ethylic hydrogen benzoïnylmalonate,  $\begin{array}{l}C_6H_5\cdot C(OH)\cdot CH<\begin{array}{l}COOC_2H_5\\COOH\end{array}\\ C_6H_5\cdot CO\end{array}$, and (2) desylenemalonic acid,  $\begin{array}{l}C_6H_5\cdot C{:}C(COOH)_2{}^*\\ C_6H_5\cdot CO\end{array}$.

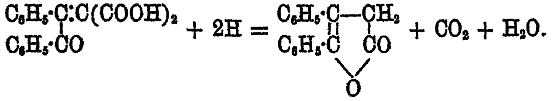
When the former compound is warmed with glacial acetic acid, it parts with water, yielding the monethylic salt of the latter.

By boiling desylenemalonic acid with fuming hydriodic acid, it is transformed into a mixture of Victor Meyer and Oelker's desylacetic acid and Klingemann's diphenylcrotolactone, carbon dioxide being eliminated in the process:



$$\begin{array}{l}C_6H_5\cdot C{:}C(COOH)_2\\ C_6H_5\cdot CO\end{array} + 2H = \begin{array}{l}C_6H_5\cdot CH\cdot CH_2\cdot COOH\\ C_6H_5\cdot CO\end{array} + CO_2;$$

Desylacetic acid.



$$\begin{array}{l}C_6H_5\cdot C{:}C(COOH)_2\\ C_6H_5\cdot CO\end{array} + 2H = \begin{array}{l}C_6H_5\cdot C - CH_2\\ C_6H_5\cdot C \quad CO\\ \quad\quad O\end{array} + CO_2 + H_2O.$$

Diphenylcrotolactone.

Diphenylcrotolactone was obtained by Klingemann (*Annalen*, 269, 134) by the dehydrating action of heat on desylacetic acid. In the present case, it might be formed either directly from desylenemalonic acid, or, indirectly, by the dehydration of desylacetic acid, the latter being the primary product of the interaction; but we did not further investigate this point.

When heated above its melting point, desylenemalonic acid parts with carbon dioxide, yielding desyleneacetic (β-benzoylcinnamic) acid,

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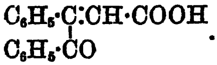
* The name "desylene," denoting the dyad group, $C_6H_5\cdot CO\cdot \underset{\cdot\cdot}{C}\cdot C_6H_5$, is formed on the analogy of Victor Meyer's "desyl," $C_6H_5\cdot CO\cdot \underset{\cdot}{C}H\cdot C_6H_5$.



$\begin{array}{l} C_6H_5\cdot C{:}CH\cdot COOH \\ \;| \\ C_6H_5\cdot CO \end{array}$. This substance was obtained in two forms, melting respectively at 150° and 169°, both of which gave, on analysis, figures agreeing with the foregoing formula; but we incline to regard this difference as due to dimorphism rather than to stereoisomerism, as the former modification, on keeping, spontaneously changed its melting point and, after a lapse of two or three weeks, melted, like the latter, at 169°. Another acid, melting at 261°, was also isolated from the product of the action of heat on desylenemalonic acid, but in quantity too small for analysis.

EXPERIMENTAL PART.

Ethylic Hydrogen Benzoinylmalonate.—Fifty grams of benzile, powdered as finely as possible, and 38 grams of ethylic malonate were introduced into a flask, after which a solution of sodium ethoxide, obtained by dissolving 5·5 grams of sodium in 65 grams of absolute alcohol,[*] was added, and the flask corked and shaken. The mixture, which turned reddish-brown on the addition of the ethoxide, became gradually thicker, until, after about an hour and a half, it formed a semi-solid mass. It was then allowed to stand for two days, during which time the colour gradually changed to a yellowish-brown. The product was shaken with ether and water simultaneously, in the hope that the ether would dissolve benzile and non-acid substances, whilst acids would be found in the aqueous solution in the form of their sodium salts; but after the mass was completely disintegrated, it was found that there was a white crystalline powder which dissolved neither in the water nor in the ether, and prevented the separation of the two liquids. The crystalline powder, which proved to be ethylic sodium benzoïnylmalonate, was separated by filtration and washed, first with cold water and then with ether.

After the removal of the solid substance, the ethereal and aqueous solutions were separated. The former yielded on evaporation nothing but benzile, half the quantity taken being in this way recovered. The aqueous solution was acidified with dilute sulphuric acid, and the copious precipitate of organic acid extracted with ether. On shaking this ethereal solution with sodium carbonate, a fresh precipitate of ethylic sodium benzoinylmalonate was produced, the quantity of which increased on standing. This precipitate was separated by filtration, treated as above, and added to the portion already obtained. We describe later on the treatment of the aqueous sodium carbonate solution, which we will distinguish as A.

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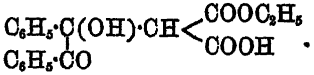
[*] If this proportion of alcohol is much exceeded, the benzile is converted mainly into ethylic benzoate and benzaldehyde.

The sparingly soluble sodium salt, of which the total yield was about 20 grams, was found to dissolve readily in hot water; but it speedily decomposed in the hot solution, benzile separating. If the solution was heated on the water bath until no more benzile separated, the filtered liquid gave no precipitate on adding sulphuric acid. It doubtless contained malonic acid produced by hydrolysis; but we did not examine it further.

In order to isolate the acid from the sodium salt, the latter was suspended in water, and, after adding dilute sulphuric acid, the mixture was shaken with ether until all the solid was dissolved. After separating the ethereal solution and distilling off the ether at a low temperature, a gummy mass was obtained which was dissolved in ethylic acetate, and light petroleum added. The substance at first separated as an oil, but, by rubbing it with a glass rod, crystallisation was induced. It formed large, lustrous, apparently rectangular prisms melting at 134°. Analysis gave figures agreeing with the formula of *ethylic hydrogen benzoïnylmalonate*,



$$\begin{array}{l} C_6H_5\cdot C(OH)\cdot CH\begin{cases} COOC_2H_5 \\ COOH \end{cases} \\ \qquad\;\, | \\ C_6H_5\cdot CO \end{array}\;.$$

0·1523 gave 0·3727 CO_2 and 0·0743 H_2O. C = 66·74; H = 5·42.
$C_{19}H_{18}O_6$ requires C = 66·67; H = 5·26 per cent.

The *ethylic sodium salt* was then regenerated from the acid ethylic salt by shaking an ethereal solution of the latter with an aqueous solution of sodium carbonate. It separated, as before, in the form of a sparingly soluble, crystalline powder, and was purified by washing it, first with cold water and then with ether. When heated at 100° it turned yellow. It was therefore dried for analysis at 40—55°.

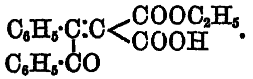
0·5983 gave 0·1177 Na_2SO_4. Na = 6·37.
$C_{19}H_{17}O_6Na$ requires Na = 6·32 per cent.

Ethylic Hydrogen Desylenemalonate.—In our first attempt to prepare the acid ethylic salt from the sparingly soluble sodium salt, we dissolved the latter in hot glacial acetic acid. On diluting the solution with water, a substance was deposited in rosettes of long, clear needles. It was purified by dissolving it in a small quantity of ethylic acetate and adding a large excess of light petroleum; from this solution it separated in rosettes of slender, lustrous prisms melting, not very sharply, at 124°. The substance was an acid, and dissolved readily in sodium carbonate; but, that it was not the acid corresponding with the sodium salt from which it had been obtained was evident, inasmuch as its sodium salt was readily soluble, and, when the solution was digested on the water bath, gave no separation of benzile.

Analysis showed that it had been formed from ethylic hydrogen benzoïnylmalonate by the abstraction of the elements of a molecule of water.

0·1401 gave 0·3611 CO_2 and 0·0642 H_2O. C = 70·29; H = 5·09.
0·1621 „ 0·4177 CO_2 „ 0·0749 H_2O. C = 70·28; H = 5·13.
$C_{19}H_{16}O_5$ requires C = 70·37; H = 4·94 per cent.

This compound is *ethylic hydrogen desylenemalonate*,



$$\underset{C_6H_5\cdot CO}{C_6H_5\cdot \overset{}{C}}{:}C<\begin{matrix}COOC_2H_5\\ COOH\end{matrix}.$$

When warmed on the water bath with sodium hydroxide, it is hydrolysed, and, on acidifying the solution, desylenemalonic acid (see following section) is precipitated.

Desylenemalonic acid.—The filtrate, A, was digested on the water bath until benzile, produced by the hydrolysis of ethylic sodium benzoïnylmalonate, ceased to separate. The solution, filtered from the benzile and acidified with sulphuric acid, gave a precipitate, which, after purifying by a process to be described later on, gave figures agreeing with those required for desylenemalonic acid.

If, however, the other compounds above described are not required, the following method gives the best yield of desylenemalonic acid. The product of the action of sodium ethoxide on a mixture of benzile and ethylic malonate, employing the proportions above given, is shaken with a mixture of ether and very dilute sulphuric acid. In this way, all the organic acids are liberated, and, along with unaltered benzile, dissolve in the ether. The ethereal solution is separated, the ether removed by distillation, and the residue dissolved in excess of glacial acetic acid. The greater part of the acetic acid is then distilled off over a free flame, any ethylic hydrogen benzoïnylmalonate being thus converted into ethylic hydrogen desylenemalonate, and water is added to the remainder. The precipitated organic substance is again dissolved in ether, and the solution shaken with an aqueous solution of sodium carbonate, to remove acids, the separated sodium carbonate solution being extracted with a fresh quantity of ether, to get rid of the last traces of benzile. The aqueous solution then contains sodium desylenemalonate and ethylic sodium desylenemalonate. In order to hydrolyse the latter, excess of sodium hydroxide is added, and the solution is digested on the water bath for some hours. It is then filtered from any resin that may have separated, after which, the desylenemalonic acid is precipitated with dilute sulphuric acid. The desylenemalonic acid is purified by dissolving it in the smallest possible quantity of ethylic acetate and adding excess of benzene, when it separates very slowly in slender, felted needles, apparently containing benzene of crystallisation.

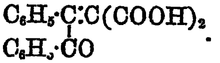
The yield from 50 grams of benzile, 38 grams of ethylic malonate, 5·5 grams of sodium, and 65 grams of alcohol was only 24 grams; but, as in the experiment already described, about half the benzile was recovered unchanged.

For most purposes, the desylenemalonic acid, thus obtained, is sufficiently pure, but it has a pale brown colour, and the melting point is not sharp. For analysis, it was purified by converting it into its sparingly soluble calcium salt, decolorising the solution by boiling it with animal charcoal, and recrystallising the salt. The acid was obtained from this salt by shaking it with a mixture of dilute hydrochloric acid and ether. The acid, left on evaporating the ether, was finally purified by recrystallisation from a mixture of ethylic acetate and benzene.

Desylenemalonic acid forms colourless, slender, felted needles, which become opaque on drying. It melts at 130°. When heated above its melting point, it evolves gas and becomes dark coloured. For analysis, it was dried at 100°.

The analytical figures agreed with the formula $C_{17}H_{12}O_5$.

0·1279 gave 0·3240 CO_2 and 0·0480 H_2O. C = 69·09; H = 4·17.
0·2040 „ 0·5155 CO_2 „ 0·0753 H_2O. C = 68·91; H = 4·10.
$C_{17}H_{12}O_5$ requires C = 68·92; H = 4·05 per cent.

It has the constitution 

$$\begin{array}{l} C_6H_5\cdot C{:}C(COOH)_2 \\ \quad\;\; | \\ C_6H_5\cdot CO \end{array}.$$

The *silver salt*,* which was prepared by precipitating the ammonium salt with silver nitrate, is very sparingly soluble in cold water, but dissolves in boiling water almost without decomposition, and is deposited in needles from the cooled solution. For analysis, it was dried at 100°.

0·1288 gave 0·0545 silver. Ag = 42·31.
$C_{17}H_{10}O_5Ag_2$ requires Ag = 42·35 per cent.

Action of Hydriodic acid on Desylenemalonic acid.—Desylenemalonic acid was boiled with excess of fuming hydriodic acid (*d* 1·96) for five minutes in a flask over a bare flame, shaking the mixture during the process. The substance fused, and iodine was given off. Water was then added, and the dark-coloured, oily, organic substance which separated was washed with water, dissolved in ether, and the ethereal solution freed from iodine by shaking it with a dilute aqueous solution of sulphurous acid. The ethereal solution was washed with water and then shaken with a solution of sodium carbonate, which extracted from it an organic acid, whilst a non-acid substance remained in the ether, and was obtained as a crystalline residue on evaporation. This non-acid substance is not very soluble in ether, and, unless a sufficiency of ether is employed, is apt to separate before the acid has been extracted.

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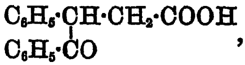
* Prepared and analysed by Mr. G. Druce Lander, B Sc.

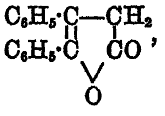
The sodium carbonate solution gave, on acidifying with dilute sulphuric acid, a precipitate of an organic acid, which was extracted with ether, and, after expelling the ether, recrystallised from hot benzene. It formed lustrous crystals, of octahedral habit, melting at 160°. Analysis of the substance, dried at 100°, gave figures agreeing with the formula $C_{16}H_{14}O_3$.*

0·1315 gave 0·3647 CO_2 and 0·0659 H_2O. $C = 75·64$; $H = 5·57$.
$C_{16}H_{14}O_3$ requires $C = 75·59$; $H = 5·51$ per cent.

This is the formula of *desylacetic acid*, 
$\begin{array}{l} C_6H_5\cdot CH\cdot CH_2\cdot COOH \\ \quad\quad\quad | \\ C_6H_5\cdot CO \end{array}$, and the melting point (160°) very nearly agrees with that found by Knoevenagel (*Ber.*, 1888, **21**, 1350) for this substance (162°). The substance was therefore compared with a specimen of desylacetic acid prepared by Knoevenagel's method (from sodio-deoxybenzoïn and ethylic iodacetate, afterwards hydrolysing the ethereal salt thus obtained), and was found to be indistinguishable from it, except that this specimen, which had been more frequently recrystallised, melted one degree higher than our acid.

The non-acid substance above referred to, which remained after expelling the ether, was recrystallised from hot benzene. It was deposited in tufts of slender needles, melting constantly at 151·5°. Analysis of the substance, dried at 100°, gave figures agreeing with the formula $C_{16}H_{12}O_2$.

0·1450 gave 0·4322 CO_2 and 0·0682 H_2O. $C = 81·29$; $H = 5·23$.
$C_{16}H_{12}O_2$ requires $C = 81·35$; $H = 5·09$ per cent.

This is the formula of *diphenylcrotolactone*, 
$\begin{array}{ccc} C_6H_5\cdot C & - & CH_2 \\ \| & & | \\ C_6H_5\cdot C & & CO \\ & \diagdown\!\diagup & \\ & O & \end{array}$, a compound formed from desylacetic acid by abstraction of water, and the melting point agrees exactly with that given by Klingemann (*loc. cit.*)

Desyleneacetic (β-Benzoylcinnamic) acid.—As a dicarboxylic acid in which both carboxyl groups were attached to the same carbon atom, it was probable that desylenemalonic acid would part with carbon dioxide when heated, yielding a monobasic acid. The evolution of gas already referred to, observed when the substance was heated above its melting point, was doubtless to be interpreted in this sense.

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* The substances used for this and the next following analysis were, we should mention, obtained by the action of hydriodic acid on the monethylic salt of desylenemalonic acid. We happened to have a quantity of this compound, and used it for the interaction without previously converting it into the acid. It is hydrolysed by the hydriodic acid, and consequently gives the same products as desylenemalonic acid itself, as we convinced ourselves by a careful comparison of the substances obtained in the two cases.

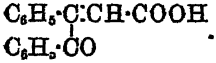
In order to obtain the monobasic acid, we at first tried the plan of distilling desylenemalonic acid under reduced pressure. From the distillate we had no difficulty in isolating an acid of the expected composition; but the yield was only one-fortieth of the weight of desylenemalonic acid taken. However, by merely heating the desylenemalonic acid until carbon dioxide ceased to be evolved, a better yield, although still a very poor one, was obtained.

The desylenemalonic acid was introduced into a tubulated distilling flask, which was exhausted during the whole operation by means of a filter-pump, in order to prevent aerial oxidation. The flask was heated in a glycerol bath at 180—200° for two hours, at the end of which time the evolution of carbon dioxide had practically ceased. The dark violet-coloured mass was dissolved in ether, and the ethereal solution shaken with aqueous sodium carbonate; the carbonate solution was acidified with dilute sulphuric acid, and the precipitated acid, after extraction with ether, purified by recrystallisation from benzene. It was found, however, that the crystals, which were large and well formed, obstinately retained a brown colour; but, by digesting them on the water bath with a small quantity of benzene, they disintegrated, forming a white powder from which the hot benzene, containing the greater part of the colouring matter, could be poured off; on dissolving this powder in more hot benzene, a solution was obtained which deposited colourless crystals, melting constantly at 169°. The yield from 25 grams of desylenemalonic acid was only 4 grams.

Analysis of a specimen prepared by the distillation method, having a faint brownish tinge, and melting at 168°,* gave figures agreeing with the formula $C_{16}H_{12}O_3$.

0·1008 gave 0·2813 CO_2 and 0·0435 H_2O. $C = 76·11$; $H = 4·79$.
$C_{16}H_{12}O_3$ requires $C = 76·19$; $H = 4·76$ per cent.

The compound is, therefore, *desyleneacetic* (*β-benzoylcinnamic*) *acid*,



$$\begin{array}{l}C_6H_5\cdot C{:}CH\cdot COOH\\ \quad\,| \\ C_6H_5\cdot CO\end{array}$$

. A compound of this formula ought to be capable of existing in two stereoisomeric forms, and we at one time thought we had actually obtained the two isomerides. A specimen of the substance, prepared by the distillation method, gave, on recrystallisation from benzene, two distinct forms, which could without difficulty be mechanically separated; clear, brownish crystals, grouped in rosettes, melting at 168° (the specimen used for the foregoing analysis); and colourless, more or less opaque, single crystals, melting at 150°. The latter gave, on analysis, $C = 75{\cdot}95$, $H = 4{\cdot}96$, showing that they had the same composition as the others. Some weeks later, the melting point of these crystals was redetermined, and was found to have risen to 169°, the melting point of the form already described. We must, therefore, regard this supposed isomeride (which we obtained only once) as an unstable crystalline form of the substance melting at 169°. Neither of the forms contained benzene of crystallisation.

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* This specimen was prepared and analysed before we had hit upon the foregoing method of purifying the substance.

The *silver salt** was obtained as a white precipitate, by adding silver nitrate to a solution of the ammonium salt. It is not decomposed by boiling with water, in which it is almost insoluble.

0·2194 gave 0·0658 silver. $Ag = 29{\cdot}99$.

$C_{16}H_{11}O_3Ag$ requires $Ag = 30\ 08$ per cent.

In the preparation of desylacetic acid by merely heating desylenemalonic acid without distilling it, a small quantity of a white crystalline acid melting at 261° was obtained. It formed a sparingly soluble sodium salt. The quantity was insufficient for further examination.

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XIX.—*Stereoisomeric αα′-Dimethylpimelic acids.*

By F. STANLEY KIPPING, Ph.D., D.Sc.

αα′-DIMETHYLPIMELIC acid was first described by the author and Mackenzie (Trans., 1891, **59**, 569), by whom it was obtained as a bye-product in the course of some experiments on the preparation of diacetylheptane, $CH_3{\cdot}CHAc{\cdot}[CH_2]_3{\cdot}CHAc{\cdot}CH_3$; this diketone being required in considerable quantities for the purpose of examining its behaviour on reduction (Kipping, Trans., 1893, **63**, 111), an alcoholic solution of trimethylene bromide was treated with ethylic sodiomethylacetoacetate, and the product—ethylic dimethyldiacetylpimelate—was hydrolysed with alcoholic potash. As is usual in such cases, the ethereal salt underwent both ketonic and acid hydrolysis, so that, in addition to diacetylheptane, αα′-dimethylpimelic acid and αα′-dimethyl-α′-acetylcaproic acid were formed, in accordance with the equations

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* Prepared and analysed by Mr. Lander.

$$\mathrm{COOEt{\cdot}CMeAc{\cdot}[CH_2]_3{\cdot}CMeAc{\cdot}COOEt + 4KOH = COOK{\cdot}CHMe{\cdot}[CH_2]_3{\cdot}CHMe{\cdot}COOK + 2C_2H_5{\cdot}OH + 2CH_3{\cdot}COOK.}$$

$$\mathrm{COOEt{\cdot}CMeAc{\cdot}[CH_2]_3{\cdot}CMeAc{\cdot}COOEt + 4KOH = CHMeAc{\cdot}[CH_2]_3{\cdot}CHMe{\cdot}COOK + 2C_2H_5{\cdot}OH + CH_3{\cdot}COOK + K_2CO_3.}$$

These two acids could not be satisfactorily separated by fractional distillation under reduced pressure, or by any of the ordinary methods, but, by taking advantage of the fact that the ammonium salt of dimethylacetylcaproic acid undergoes dissociation in boiling aqueous solution, whereas the neutral ammonium salt of dimethylpimelic acid is converted into the ammonium hydrogen salt, their separation was easily accomplished; for this purpose, it was only necessary to dissolve the mixture in ammonia, boil the solution until ammonia ceased to be evolved, and then extract the dimethylacetylcaproic acid with ether. The aqueous solution of ammonium hydrogen dimethylpimelate was then acidified, and the organic acid extracted by again shaking with ether; the yellow, or brown, oily dimethylpimelic acid which remained on evaporating the ethereal solution was further purified by fractional distillation under reduced pressure, and finally by recrystallisation.

Dimethylpimelic acid was also obtained, in a somewhat different manner, by the author and Mackenzie, namely, by the hydrolysis of its ethylic salt, a compound which was directly produced in large quantities when the alcohol employed in the preparation of ethylic dimethyldiacetylpimelate was not sufficiently free from water; the crude acid, obtained in this manner, was less impure than that separated from the dimethylacetylcaproic acid, and solidified more readily and completely, but not until it had been fractionally distilled under reduced pressure.

The crystalline dimethylpimelic acid, prepared by these methods, did not melt at all sharply, and very great difficulty was experienced in recrystallising it, as it was almost invariably deposited from solvents in an oily condition; ultimately, however, it was obtained in transparent crystals, melting sharply at 80—81°.

A few months after the publication of these observations, a paper by Perkin and Prentice, containing an account of pimelic acid and its homologues—and amongst them *αα'*-dimethylpimelic acid—was communicated to the Society (Trans., 1891, **59**, 818). These acids were prepared by treating ethylic pentanetetracarboxylate with sodium ethoxide and an alkyl iodide in alcoholic solution,

$$\mathrm{(COOEt)_2CNa{\cdot}[CH_2]_3{\cdot}CNa(COOEt)_2 + 2RI = (COOEt)_2CR{\cdot}[CH_2]_3{\cdot}CR(COOEt)_2 + 2NaI,}$$

hydrolysing the products, and then decomposing the resulting tetracarboxylic acids by heating them at 200—220°,

$$(COOH)_2CR{\cdot}[CH_2]_3{\cdot}CR(COOH)_2 = COOH{\cdot}CHR{\cdot}[CH_2]_3{\cdot}CHR{\cdot}COOH + 2CO_2.$$

The αα′-dimethylpimelic acid which they thus obtained should obviously have been structurally identical with the acid described by the author and Mackenzie, and, as a matter of fact, in most respects, the properties of the two preparations appeared to be very similar; the boiling point of the ethylic dimethylpimelate prepared by Perkin and Prentice was also practically the same as that of the ethylic salt which had been described by the author and Mackenzie. In one important point, however, there was disagreement as regards the properties of the acid, inasmuch as Perkin and Prentice found its melting point to be 74—76°, and, in spite of repeated recrystallisation, they were unable to observe any alteration or any further approximation to the melting point (80—81°) given by the author and Mackenzie.

The two papers already referred to were closely followed by a third, in which an account of αα′-dimethylpimelic acid was given by Zelinsky (*Ber.*, 1891, **24**, 3997), who, apparently, was unaware of the results which had been published by the author and Mackenzie. Zelinsky prepared αα′-dimethylpimelic acid by treating ethylic α-cyanopropionate with sodium ethoxide and trimethylene bromide,

$$2COOEt{\cdot}CMeNa{\cdot}CN + C_3H_6Br_2 = COOEt{\cdot}CMe(CN){\cdot}[CH_2]_3{\cdot}CMe(CN){\cdot}COOEt + 2NaBr,$$

hydrolysing the product with potash, and warming the tetracarboxylic acid with concentrated sulphuric acid until it was converted into αα′-dimethylpimelic acid; this compound was separated from accompanying oil, and the melting point, "der vollständig gereinigten Krystalle," was found to be 71—73°. The oily mother liquor from these crystals did not solidify, and, on analysis, gave the same results as the crystalline acid; Zelinsky suggested, therefore, that the oil might be a stereoisomeride of the compound melting at 71—73°, but, owing to lack of material, he was unable to support this view by any further evidence.

These later determinations of the melting point of dimethylpimelic acid not only differed from one another, but also from that given by the author and Mackenzie, and to such an extent that the discrepancies could hardly be assigned to the slight and almost unavoidable differences in observation; at the same time, the differences were not large enough, and there was altogether insufficient evidence of any kind, to warrant the conclusion that the three preparations in question were not identical.

Under these circumstances, a more exhaustive investigation of $\alpha\alpha'$-dimethylpimelic acid was eminently desirable, firstly, in order to confirm or disprove the accuracy of previous observations, and, secondly, in order to ascertain whether this acid, like all the lower substituted acids of the same series, exists in stereoisomeric forms.

The results arrived at may be summarised as follows.

$\alpha\alpha'$-Dimethylpimelic acid exists in two stereoisomeric modifications melting at 81—81·5° and 76—76·5° respectively, and the crude crystalline acid obtained by hydrolysing ethylic dimethyldiacetylpimelate is a mixture of these stereoisomerides. The acid of higher melting point—which may be termed the *para*-acid—is easily obtained from this mixture in a pure condition by fractional crystallisation, but the *anti*-acid—the modification of lower melting point—cannot be directly isolated, at any rate when operating with moderately small quantities.

The two modifications are most conveniently separated with the aid of their anilides; the anilide of the para-acid melts at 183—184°, that of the anti-acid at 154—155°, and, on hydrolysis with dilute alcoholic hydrochloric acid, each is reconverted into the modification from which it is derived.

The two acids differ in crystalline form and in solubility, but, on the whole, they are very similar in all ordinary properties, and they have the same electrical conductivity. The difference in melting point is remarkably small, very much smaller in fact than in the case of the two stereoisomeric forms exhibited by other acids of this series having a similar constitution, as will be seen from the following table.

	Para.	Anti.	Diff.
Dimethylsuccinic acid....	192—194°	120—123°	72°
Dimethylglutaric acid...	128	103	25
Dimethyladipic acid.....	142	70—72	71
Dimethylpimelic acid....	81—81·5	76—76·5	5

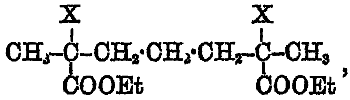
Now, since dimethylpimelic acid is the highest member of this particular dimethyl-series, and its two modifications show the smallest difference in melting point, it might be expected that, for this and other reasons, the two modifications of such acids would show a continually diminishing difference with increasing molecular weight; so far, however, there is little evidence of any such regularity, at any rate in melting point, as the two modifications of dimethylglutaric acid differ by only 25°, those of dimethyladipic acid by as much as 71°.

As regards electrical conductivity, on the other hand, there is a marked regularity on passing up the series, and the two modifications of dimethylpimelic acid, like those of the next two lower members, have the same dissociation constant.

	Dimethylsuccinic acid.	Dimethylglutaric acid.	Dimethyladipic acid.	Dimethylpimelic acid.
Para. K =	0·0190	0·0055	0·0042	0·00343
Anti. K =	0·0122	0·0055	0·0042	0·00344

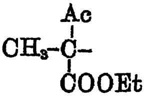
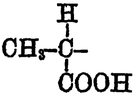
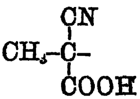
Both modifications of $\alpha\alpha'$-dimethylpimelic acid, the anti-form more especially, have a very great tendency to remain in the liquid condition unless they are in a state of great purity; the pure compounds, however, may be recrystallised without difficulty, and, under suitable conditions, may be obtained in forms which allow of goniometrical measurement. The crystallographic examination was kindly undertaken by Mr. W. J. Pope, and the results, which are given below, afford a valuable, and by no means superfluous, proof of the non-identity of these, otherwise so similar, modifications.

A comparison of the properties of anti-dimethylpimelic acid (m. p. 76—76·5°) with those of the dimethylpimelic acid (m. p. 74—76°), described by Perkin and Prentice, leaves little doubt as to the identity of these two compounds, and since this particular modification is by far the more readily soluble of the two, it is highly improbable that the para-acid could have been present in Perkin and Prentice's preparation and yet have escaped notice; this conclusion, moreover, is borne out by the fact that only one modification was obtained by them in the case of all the substituted pimelic acids prepared in a similar manner. That two methods of preparation, namely, that of Perkin and Prentice on the one hand, and that of the author on the other, should lead to such different results is at first sight remarkable, because in both cases the acid was obtained by substituting hydrogen for a group X in an ethereal salt of the constitution



$$CH_3\text{–}\underset{COOEt}{\overset{X}{C}}\text{–}CH_2\cdot CH_2\cdot CH_2\text{–}\underset{COOEt}{\overset{X}{C}}\text{–}CH_3,$$

yet, when X = –COOEt, only the anti-acid was formed, whereas, when X = $-CO\cdot CH_3$, both modifications were produced. The explanation of this difference probably lies in the fact that the two asymmetric carbon atoms, upon which the existence of the two stereoisomerides is assumed to depend, originated under very different conditions; in one case, asymmetry was not established until two of the carboxyl groups of the tetracarboxylic acid were displaced by two hydrogen atoms—a change which was accomplished by heating at 200—220°; in the other the asymmetric carbon atoms originated in alcoholic solution at a comparatively low temperature. There is also this further difference between the two modes of preparation, that whereas Perkin and Prentice obtained their acid directly from a compound which could not itself exhibit stereoisomerism, the mixture of the anti- and para-acids was produced from a substance which should itself exist in stereoisomeric forms. Arguments of this kind may not perhaps be generally applicable, but they certainly show that in this particular case the two methods of preparation are really not so similar as they appear to be, and do not, therefore, necessarily yield identical products. Such considerations may also be of value in elucidating the nature of the two isomerides in question, because, as the acid melting at 76—76·5° is the one which is produced by changes occurring at a high temperature, it is probably the internally compensated, and not the racemic modification.

On comparing Zelinsky's method of preparation with that employed by the author, it is evident that the conditions under which the asymmetric carbon atoms of the dimethylpimelic acid originated are practically identical, the main difference between the two processes being, in fact, that, whereas the conversion of the  $CH_3{-}\overset{Ac}{\underset{COOEt}{C}}{-}$ groups of ethylic dimethyldiacetylpimelate into  $CH_3{-}\overset{H}{\underset{COOH}{C}}{-}$ groups was accomplished in boiling alcoholic solution, the substitution of hydrogen for the cyanogen radicles in the groups  $CH_3{-}\overset{CN}{\underset{COOH}{C}}{-}$ was effected by Zelinsky by heating the ethylic salt with alcoholic potash, and then warming with sulphuric acid (at a temperature not stated). It seems probable, therefore, that identical products should have been obtained by the two methods, and that Zelinsky's acid (m. p. 71—73°) was in reality a mixture of the two stereoisomerides; this conclusion is borne out by the fact that in the case of $\alpha\alpha'$-dimethylglutaric acid (Zelinsky, *Ber.*, 1889, **22**, 2823) and of $\alpha\alpha'$-dimethyladipic acid (Zelinsky, *Ber.*, 1891, **24**, 3997)—both of which were prepared by methods essentially identical with that used in the case of $\alpha\alpha'$-dimethylpimelic acid—mixtures of the two modifications were obtained. It is not impossible that the acid prepared from ethylic dimethyldiacetylpimelate may have undergone change on distillation under reduced pressure, the one modification having been partially converted into the other; such an assumption would doubtless explain away the difficulties, but it has no basis in fact, and is not warranted by the results of experiments described below; nevertheless, it cannot be dismissed as impossible.

Isolation of Para-dimethylpimelic acid.

The dimethylpimelic acid employed in these experiments was prepared by the hydrolysis of ethylic dimethyldiacetylpimelate (Kipping and Mackenzie, *loc. cit.*), and was separated from the dimethylacetylcaproic acid by the method already mentioned. The crude acid was dark brown, and as it showed no signs of crystallising, even on keeping for a long time over sulphuric acid, it was distilled under reduced pressure. The two principal fractions were those collected between 245° and 250° and between 250° and 255° (50 mm.), but a considerable quantity passed over below 245°, and a small quantity of a tar-like oil remained in the distilling flask.

Those fractions which deposited crystals were filtered with the aid of the pump, and the residue spread on porous earthenware, on which it was left until it became quite hard and could be readily reduced to a fine powder without caking; the oily filtrate was again placed over sulphuric acid, but only a trace of a crystalline deposit was formed even after several months had elapsed.

The first point which required attention was, whether dimethylpimelic acid melted at 80—81°, as previously stated by the author and Mackenzie. A portion of the fine powder was therefore recrystallised from light petroleum (b. p. 50—60°) containing a very small proportion of benzene, the addition of which tended to prevent the separation of the acid in an oily condition; the first crystallisation gave a deposit melting at 58—63°, but after numerous operations, which extended over several weeks, the melting point of the most sparingly soluble portion rose to 72—73°; at this stage, the substance was obtained in what seemed to be definite crystals, but, on further recrystallisation from light petroleum, its melting point rose about 1° with each operation, and finally reached 81°. This preparation was then successively recrystallised from cold water, petroleum, cold water, and a mixture of petroleum with benzene, but the last, and most sparingly soluble, fraction melted, as before, at 81—81·5°.

A sample of this compound was then analysed.

0·1519 gave 0·3212 CO_2 and 0·1177 H_2O. C = 57·63; H = 8·61.
$C_9H_{16}O_4$ requires C = 57·44; H = 8·51 per cent.

A portion of the same sample was titrated against alkali.

0·0938 gram neutralised 9·65 c.c. of sodium carbonate solution, 1 c.c. of which was equivalent to 0·009675 gram of dimethylpimelic acid; quantity found = 0·0934.

These analyses, and the method of preparation of the compound, show it to be $\alpha\alpha'$-dimethylpimelic acid, and the melting point previously given is therefore confirmed; the properties of this acid are described later.

Examination of Mother Liquors.—The crystals deposited from the various portions of the mother liquors, from which the acid melting at 81—81·5° had separated, were now examined in order, if possible, to isolate an isomeride, but all attempts in this direction were unsuccessful; although fractions melting as low as 58—64° and as high as 75—77° could be separated without much difficult, the melting point invariably altered on recrystallising, and finally the portions became so small that it was of little use continuing the process.

Attempts were then made to effect a separation by fractional crystallisation from cold water, and in this way a considerable quantity of a substance melting fairly sharply at 74—76° was finally obtained from the more readily soluble portions; it is probable that this preparation consisted essentially of the anti-acid, but as the melting point of this isomeride was at that time unknown, the fraction in question was thought to be a mixture and the experiments were discontinued.

The appearance and behaviour of the numerous samples of acid obtained in the above operations certainly led to the conclusion that the original substance was a mixture of stereoisomerides, but before proceeding further in the attempts to isolate the unknown modification some preliminary evidence of its existence was desirable. For this reason, a portion of the crystalline powder melting at 56—60° was dissolved in light petroleum, the filtered solution evaporated, and the residue kept for two days over sulphuric acid under reduced pressure; an analysis and a titration of this substance—a colourless oil—gave practically the same results as those obtained with a sample of the pure para-acid. This fact clearly indicated the presence of an isomeride of the latter, as it was improbable that any other substance could be present in sufficient quantity to lower the melting point from 81° to 60°, and yet have no effect on the results of the analyses.

On this assumption, the experiments were continued, and in the first place various salts were prepared from the crude mixture of acids; in all cases, however, these salts were badly characterised, and quite unsuitable for the end in view.

The conversion of one of the modifications of acids of this kind into the other may, as is well known, be frequently brought about by heating with hydrochloric acid, and apparently the intermediate formation of an anhydride is by no means a necessary step in the process, since this treatment has been found to be applicable in the case of dimethyladipic acid (Zelinsky, *Ber.*, 1891, 24, 3997); if then one of the dimethylpimelic acids in the mixture could be thus transformed into the other modification, the product might be the unknown anti-acid.

A portion of the oil, which had been separated from the crystalline acid as described above, was heated with about 20 parts of moderately concentrated hydrochloric acid at 200—220° for about 10 hours; there was slight pressure on opening the tube, and the acid had charred, yielding decomposition products which had an odour of petroleum. The solution was extracted with ether, and the brown oil, obtained on evaporating the extract, was placed in a desiccator, where it gradually solidified; after freeing the crystalline mass from oil with the aid of porous earthenware, it was first dissolved in benzene and treated with animal charcoal, and then recrystallised from light petroleum. The several fractions obtained in this way melted at very different temperatures, ranging from about 60° to about 76°, but it was found to be impossible to isolate any definite substance with the quantity at disposal; it would seem, therefore, that a complete conversion of one isomeride into the other had not taken place, although apparently this change had occurred to some extent, as the mixture solidified so much more readily after the treatment than before. A portion of the oily mixture was also heated alone at 190—200° for about six hours, but this experiment was equally unsuccessful, as the product could not be got to crystallise.

Preparation and Separation of Stereoisomeric Anilides.

The great difficulty experienced in the attempts to separate the two acids by fractional crystallisation was due almost entirely to the fact that the mixture was so frequently deposited from its solution as an oil, even when evaporation took place very slowly at the ordinary temperature; as the separation of the corresponding anilides would probably be free from this difficulty, a portion of the crystalline mixture and a portion of the oil were separately treated with a slight excess of the theoretical quantity of phosphorus pentachloride. The oils thus produced were heated for some time at about 100° in a stream of dry air, in order to expel most of the phosphorus oxychloride, and were then slowly poured into excess of dry aniline; the pasty products were heated for a short time on the water bath to complete the action, and then extracted with warm dilute hydrochloric acid to remove the excess of aniline; the solid residues were finally submitted to fractional crystallisation from hot dilute alcohol and ethylic acetate.

The first product which was isolated melted at about 208°, and proved to be a phosphorus compound—probably the anilide of phosphoric acid, $PO(NH{\cdot}C_6H_5)_3$, which melts at 208°—produced from the phosphorus oxychloride which was not completely expelled, but on further crystallisation a crystalline anilide free from phosphorus was obtained. This compound melted at 183—184°, and gave, on analysis, results agreeing well with those required by the anilide of dimethylpimelic acid.

0·1614 gave 0·4400 CO_2 and 0·1170 H_2O. C = 74·35; H = 8·05.
$C_{21}H_{26}N_2O_2$ requires C = 74·56; H = 7·69 per cent.

The mother liquors from this anilide, on further treatment, yielded fractions of much lower melting point, and also a considerable quantity of a brown oil, which solidified only very slowly; from these portions, but only after repeated recrystallisation from various solvents, a substance melting at 154—155° was isolated.

This compound, which proved to be isomeric with the anilide melting at 183—184°, gave the following result on analysis.

0·1310 gave 0·3579 and 0·0951. C = 74·51; H = 8·06.
$C_{21}H_{26}N_2O_2$ requires C = 74·56; H = 7·69 per cent.

After separating these compounds as completely as possible, crystalline deposits were obtained, some of which, though quite colourless and free from oil, melted as low as 130—135°; these fractions doubtless consisted in the main of the anilide melting at 154—155°, but, although free from any phosphorus compound, and apparently also from the anilide melting at 183—184°, they contained some other substance the nature of which could not be determined; it was the presence of this unknown substance which rendered the isolation of the second anilide a matter of some difficulty, a mixture consisting only of the anilides of the two dimethylpimelic acids being very readily resolved into its components by fractional crystallisation from hot dilute alcohol.

Both the samples of crude anilides prepared from the crystalline and oily acids respectively, were found to be mixtures, but that obtained from the crystalline acid contained a relatively larger proportion of the anilide melting at 183—184°.

Reconversion of the Anilides into the Acids.

Having obtained the two anilides in a state of purity they were separately reconverted into the corresponding acids, firstly in order to ascertain which was the derivative of the para-acid, and secondly in order to obtain the stereoisomeric anti-acid.

The pure anilide melting at 154—155° was dissolved in a little hot dilute methylic alcohol, a small quantity of concentrated hydrochloric acid added, and the solution heated to boiling in a reflux apparatus until the addition of water produced no perceptible turbidity; this operation occupied about 20 hours. The solution was then repeatedly evaporated on the water bath until free from hydrochloric acid, the residue dissolved in a small quantity of water, the solution filtered from traces of a brown oil (probably slightly impure acid), and the colourless filtrate evaporated to dryness. The pasty residue was then dried at 100°, extracted with boiling light petroleum, and the filtered extract evaporated. The crystalline powder insoluble in petroleum was proved to be aniline hydrochloride by the usual tests, thus affording further evidence that the substance melting at 154—155° was an anilide.

The oily acid obtained on evaporating the light petroleum extract was dissolved in water, and the solution left at the ordinary temperature; oily drops separated in the course of a few days, but on rubbing with a glass rod they gradually solidified, and on further evaporation over sulphuric acid the rest of the acid was deposited in colourless crystals; these melted at 73—75°, but on recrystallisation from water their melting point rose to, and became constant at, 76—76·5°.

The anilide melting at 183—184° was also hydrolysed with dilute alcoholic hydrochloric acid exactly in the manner just described; it yielded aniline hydrochloride, and an acid which melted at 81—81·5°.

There are, therefore, two stereoisomeric $\alpha\alpha'$-dimethylpimelic acids; the para-acid melts at 81—81·5°, and its anilide at 183—184°, whereas the anti-acid melts at 76—76·5°, and its anilide at 154—155°.

Properties of the Stereoisomeric Acids.

A short description of para-dimethylpimelic acid has been previously given (Kipping and Mackenzie, *loc. cit.*, p. 578), but several new facts have been established in the course of these experiments. The pure acid separates from tepid water in beautiful, fern-like crystals; and when crystallisation takes place slowly at the ordinary temperature it is deposited in aggregates of large opaque prisms, or in beautiful, highly lustrous and transparent, rhombic or six-sided plates (see below). It may also be recrystallised from light petroleum or from a mixture of light petroleum and benzene, but the crystals obtained under these conditions (compact prisms) are not very suitable for crystallographic examination.

The solubilty of the para-acid in water was determined with the following results.

2·7630 grams of a solution, saturated at 15°, gave, on evaporation, 0·0315 gram of the acid; 100 parts of water at 15° dissolve, therefore, 1·15 parts of the acid.

5·5547 grams of a solution, saturated at 15°, gave, on evaporation, 0·0662 gram of acid; 100 parts of water at 15° dissolve, therefore, 1·19 grams of acid.

Dr. J. Walker very kindly measured the electrial conductivity of the two stereoisomerides, and obtained the following results.

Para-dimethylpimelic acid (m. p. 81—81·5°).... K = 0·00314
Anti-dimethylpimelic acid (m. p. 76—76·5°).... K = 0·00313

Both specimens, Dr. Walker stated, gave excellent measurements, a fact which indicated a high state of purity.

The white, opaque prisms, usually obtained on evaporating a cold aqueous solution of the para-acid, are 4 or 5 mm. in length, and their edges and corners are quite transparent, the opacity of the mass being due to fern-like inclusions. The forms ordinarily shown are *c*{001} and *m*{110}; more rarely the pinacoid *a*{100} is present as a narrow strip. The acid condenses on volatilisation in tablets flattened in the direction of the *c*-axis; crystals of the same kind are sometimes obtained on crystallisation from water, and seem to consist of the forms *c*{001}, *p*{111}, and *q*{111} (see Fig. 1). Through the basal pinacoid of these, the extinction bisects the angles, and an optic axis is seen emerging in the plane *b*{010}; under a $\frac{1}{12}$th oil immersion objective, the optic axis is seen emerging almost in the centre of the field. The double refraction and the dispersion are weak. These crystals do not lend themselves readily to measurement, the faces being extremely conchoidal in character, and giving multiple images on the goniometer. A few better-developed, transparent crystals, about $\frac{1}{2}$ mm. long and $\frac{1}{8}$ mm. broad, were obtained, by allowing the aqueous solution to evaporate spontaneously over sulphuric acid. These were rhombohedral in shape, showing the forms *c*{001}, *m*{110}, and sometimes *a*{100} (see Fig. 2); one crystal which showed a face of the form *p*{11̄1} was found amongst these. The crystals belong to the monosymmetric system; the faces were all very conchoidal in character, and the measurements made on the crystals cannot be regarded as very accurate. The forms *c*{001} and *m*{110} are of about

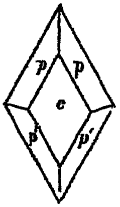


FIG 1.

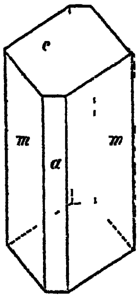


FIG. 2.

the same size, whilst $a\{100\}$ is always very much smaller. The crystals have a quartz-like lustre, but no characteristic cleavage; the refractive index is about the same as that of cedar-wood oil. These crystals are of the same kind as those described above, the optic axis always being visible through the pinacoïd *c*.

Crystalline System—Monosymmetric.

$$a : b : c = 1{\cdot}263 : 1 : 1{\cdot}062.$$
$$\beta = 43^\circ\ 23'.$$

Forms present:

a .... $\{100\}$.
c .... $\{001\}$.
p .... $\{11\bar{1}\}$.
m.......... $\{110\}$.

Angle.	No.	Limits.	Mean.	Calc.
$mm = 110 : 1\bar{1}0$	21	80° 6′— 83° 50′	81° 53′	—
$mm = 110 : \bar{1}10$	18	95 10—100 48	98 32	98° 7′
$mc = 110 : 001$	15	54 48— 58 24	56 42	—
$mc = 110 : 10\bar{1}$	11	120 36—129 41	124 47	123 18
$ac = 100 : 001$	4	40 16— 44 41	42 51	43 23
$ac = 100 : 00\bar{1}$	5	135 7—137 52	136 49	136 37
$mp = 110 : 11\bar{1}$	1	—	55 36	56 0
$pc = 11\bar{1} : 00\bar{1}$	1	—	67 18	—

On melting the crystalline substance on a microscope slide, putting on a cover glass and allowing to cool, the acid crystallises readily from centres giving a transparent product which sometimes shows an optic axis. Tiny bubbles are seen in the mass along the lines of junction of the various individuals; the substance may be easily recognised by this peculiarity. The crystalline form of the solidified magma is the same as that of the crystals obtained from aqueous solution or by volatilisation.

Anti-dimethylpimelic acid, even when pure, frequently separates from cold water as an oil; if, however, a crystal is introduced as soon as oily drops are observed, and the solution is then left for some days, the acid separates in beautiful rosettes or clusters of concentrically grouped spear-shaped crystals, which float at the surface of the liquid with the points projecting downwards; this behaviour is very characteristic, and the crystals are quite different in appearance from those of the para-acid. All other ordinary solvents, with the exception of light petroleum, dissolve the anti-acid so readily that it cannot well be recrystallised from any of them.

The solubility of this acid was determined with the following result: 2·1389 grams of an aqueous solution, saturated at 15°, gave, on evaporation, 0·0472 gram of acid; 100 parts of water at 15° dissolve, therefore, 2·206 parts of acid.

This result is practically the same as that obtained by Perkin and Prentice with their dimethylpimelic acid (m. p. 74—76°), inasmuch as they found the solubility to be 2·19 parts in 100 of water at 13·5°; it affords, therefore, confirmatory evidence of the identity of the two compounds.

The metallic salts of anti-dimethylpimelic acid are apparently identical with those of the para-acid, as, on adding solutions of copper sulphate, ferric chloride, and mercuric chloride to a solution of the ammonium salt, precipitates identical in appearance with those obtained in the case of the para-acid (*loc. cit*) were produced; barium chloride and lead acetate also gave no precipitate in moderately concentrated solutions of the anti-acid, just as with the para-acid.

The crystals of the anti-acid produced by slow evaporation of its pure aqueous solution over sulphuric acid are tiny, flattened, transparent needles about 0·5 mm. in length and 0·1 mm. in diameter. These crystals belong to the orthorhombic system, and show the forms *m*{110} and *p*{101}; the faces are much pitted by re-solution, and were only measured with difficulty. The faces of the form *m*{110} are always much smaller than those of *p*{101}; the two faces of the latter give the crystal a wedge-shaped appearance, and meet in a rounded knife-edge, through which six or seven sets of interference-spectra are visible between crossed nicols. The crystals never show the two ends complete, as they always grow in rosettes of four or five individuals, and have to be detached for measurement; only two faces of the form *p*{101} are found on each crystal. On examining the crystal through the face (101), in convergent polarised light, under a $\frac{1}{12}$th oil immersion objective, a well-defined orthorhombic interference figure of large axial angle is seen; the figure is not quite central owing to the fact that the plate is wedge-shaped. The axis *a* is the acute bisectrix, and the optic axial plane is parallel to the pinacoid *b*; the double refraction is positive and moderately weak, whilst the dispersion is weak.

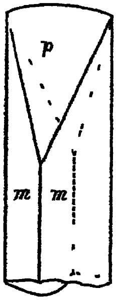


FIG. 3.

Crystalline System—Orthorhombic.

$a : b : c = 0·8207 : 1 : 2·862.$

Forms present:

m..........	{110}.
p..........	{101}.

Angle.	No.	Limits.	Mean.	Calc.
$mm = 110 : \bar{1}10$	16	99° 15′—103° 8′	101° 15′	101° 45′
$mm = 110 : 1\bar{1}0$	16	75 20 — 81 37	78 40	—
$pp = 101 : \bar{1}01$	12	143 16 —152 31	148 0	—
$pp = 101 : 10\bar{1}$	7	30 24 — 37 19	33 12	32 0

On fusing a little of the acid on a microscope slide and subsequently cooling, it solidifies slowly, crystallisation proceeding from centres as in the case of the acid melting at 81°; no small bubbles are to be seen in the mass as in the preceding case, and on examining the product microscopically it is seen that the crystals are of the same kind as those obtained from water. The acute bisectrix is perpendicular to the slide, so that the bi-axial interference figure is seen through it in all parts of the plate. On volatilisation, the acid solidifies in rosettes or ill-defined plates which always show the characteristic bi-axial interference figure.

The fact that these two acids are different is proved beyond all doubt by the crystallographic evidence alone; the one acid is always obtained in monosymmetric crystals, whilst the other invariably crystallises in the orthorhombic system.

The remarkably small difference in melting point between the two stereoisomeric acids, and the fact that except as regards solubility the two modifications presented no well-marked points of difference, rendered further evidence of their non-identity desirable, particularly as their crystallographic character had not at the time been examined; it seemed not impossible that although the two acids had been prepared from what were certainly different anilides, the compound melting at 76—76·5° might be impure para-acid, formed during the hydrolysis of the anilide with alcoholic hydrochloric acid—a process which had been necessarily rather prolonged. This doubt was set at rest by the following experiment: An intimate mixture of approximately equal portions of the two acids melting at 76° and 81° respectively, was found to soften distinctly at 55° and to liquefy completely just below 70°; after having been kept for about two days, the liquid mixture had solidified, and, when re-heated, it sintered distinctly at about 52°, melting completely at 65°; such a result could not have been obtained had the acid melting at 76° been an impure preparation of the para-modification.

The conversion of one of the modifications of the acid into the other, although doubtless capable of being accomplished by some of the methods ordinarily employed in such cases, has, unfortunately, not been effected in the present instance, owing to lack of material, and only one experiment with this object in view was made. In order to settle the question previously raised, whether distillation under reduced pressure caused any change in the original acid prepared from ethylic dimethyldiacetylpimelate, small quantities of the two pure stereoisomerides were separately heated at about 250—260° for at least 10 minutes; that is to say, the two acids were heated under practically the same conditions as were employed in the original distillation. In both cases a certain amount of decomposition occurred, as was shown by the slight darkening in colour, and vapours were evolved in fairly large quantity causing the formation of a layer of oil on the cooler parts of each of the vessels; in both cases this oily layer very soon solidified to a mass of beautiful crystals. Those obtained from the para-acid consisted of six-sided or rhombic plates belonging to the monosymmetric system, and were found to be identical with the crystals of the para-acid deposited from aqueous solution; those produced from the anti-acid consisted of isolated clusters or rosettes of spear-shaped orthorhombic prisms identical with the crystals of the anti-acid obtained from aqueous solution; in both cases, moreover, the condensate appeared quite homogeneous, indicating that no change of one modification into the other had occurred. The whole of the two samples which had been thus treated were separately recrystallised from cold water; the para-acid then melted at 73—77°, the anti-acid at 68—72°, but this was apparently due to minute traces of their decomposition products and not to the presence of the isomeride, since the crystals were well defined, and appeared to be homogeneous under the microscope. Although, therefore, not quite conclusive, this experiment shows that even if one form is converted into the other at about 250°, the change takes place very slowly.

Properties of the Stereoisomeric Anilides.

The anilide of para-dimethylpimelic acid is much more sparingly soluble in dilute alcohol than the anilide of the anti-acid, and also differs from the latter in appearance, so that the two compounds are very easily separated. The para-anilide crystallises from ethylic acetate, alcohol, and acetone in long, flattened prisms or needles, which are colourless and opaque; it is only moderately soluble in cold ethylic acetate and in cold alcohol, but readily in hot alcohol and acetic acid.

The crystals obtained from solution melt sharply at 183—184°, but when the capillary tube is withdrawn and again placed in the hot acid the solidified substance does not melt until the temperature rises to 187—188°; this curious behaviour indicates the existence of two crystalline forms, but even after keeping for four days at the ordinary temperature, the specimens which had been once melted, liquefied again at 187—188°, and not at 183—184°.

The anilide of anti-dimethylpimelic acid is very readily soluble in ethylic acetate, acetic acid, alcohol. and benzene, but rather sparingly in ether, and practically insoluble in cold light petroleum. It separates from cold dilute alcohol in curious, colourless, pear-shaped masses composed of extremely minute needles or prisms; these forms are highly characteristic, and totally different in appearance from the crystals of the para-anilide. The melting point of this anti-anilide is 154—155°.

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XX.—*Preparation of Adipic acid and some of its Derivatives.*

By Walter H. Ince, Ph.D., Demonstrator of Chemistry at St. Thomas's Hospital.

In the course of an investigation of some derivatives of adipic acid and their condensation products, large quantities of the acid were required, but as Wislicenus' method (*Annalen*, 1867, **144**, 221) of preparing it, namely, heating β-iodopropionic acid with silver, was found to be tedious and unsatisfactory, other methods were investigated. According to Laurent (*Ann. Chim. Phys.*, [2], **66**, 166), Bromeis (*Annalen*, 1840, **35**, 105), and Malaguti (*Ann. Chim. Phys.*, 1846, [3], **16**, 84), adipic acid is easily prepared by oxidising fats with nitric acid, sebacic acid being formed as an intermediate product; in fact, a method of obtaining adipic acid from sebacic acid by oxidising the latter with nitric acid is given in detail by Arppe (*Zeit. f. Chem.*, 1865, 300). The following is an account of my attempts to prepare adipic acid by these methods.

Action of Nitric acid on Sebacic acid.—Witt's method (*Ber.*, 1874, **7**, 220) for preparing sebacic acid gives very satisfactory results. Castor oil is saponified with sodium hydroxide, and the soap obtained is heated until the evolution of octylic alcohol ceases; it is then dissolved in water, and the acid precipitated by means of hydrochloric acid.

Arppe (*loc. cit.*) states that he oxidised sebacic acid by heating it with nitric acid, expelled the excess of the latter, and crystallised the residue from hot water. The crystals, after being dried and heated until they fused, were powdered when cold and then shaken with ether, which readily dissolves the adipic acid, but not the succinic acid, as the latter is insoluble in ether.

On heating sebacic acid on a water bath for four hours with a mixture of equal parts of nitric acid (sp. gr. 1·5) and water, driving off the nitric acid, and shaking the dried, powdered residue with a small amount of ether, part of it was dissolved, and the residue left on evaporating the solution to dryness was purified by recrystallisation from water. It formed colourless plates melting at 127°. On adding more ether, the remainder of the product dissolved, and from this solution crystals were obtained identical in appearance and crystalline form with the first fractions and with the original acid; and they all melted at 127°. Nitric acid, therefore, of this strength has no action on sebacic acid.

The same specimen of sebacic acid was now heated on a water bath for four hours with a more concentrated acid, namely, nitric acid diluted with half its volume of water. In this case, also, no oxidation took place.

Sebacic acid was then heated on a water bath for 48 hours [illegible]h fuming nitric acid; on allowing the liquid to cool, flat, colou[illegible]s plates were deposited which were collected and washed first [illegible]h dilute nitric acid and then with water, and finally recrystallised f[illegible] hot water; the flat crystals which were deposited melting at 127°. The strongly acid mother liquor was then evaporated to dryness, and the residue dissolved in boiling water and allowed to crystallise; these crystals also melted at 127°. Their identity with sebacic acid was established by a combustion.

0·2578 gave 0·5598 CO_2 and 0·2095 H_2O. C = 59·2; H = 9·03.
$C_{10}H_{18}O_4$ requires C = 59·41; H = 8·91 per cent.

It was thus shown that sebacic acid is not oxidised by boiling with nitric acid, but crystallises out unchanged.

Oxidation of Sebacic acid by Potassium Permanganate.—Sebacic acid is slowly oxidised by potassium permanganate in neutral, alkaline, and acid solutions; the yield, however, was so small in each case as to preclude investigation. With neutral permanganate, a faintly acid substance was obtained melting at 104—112°. The silver salt prepared by precipitating a neutral solution of the ammonium salt with silver nitrate, gave 28 8 per cent. of silver on analysis. (Adipic acid requires Ag = 60 0 per cent.) With acid and alkaline permanganate, faintly acid substances were obtained which gave no sharp melting point.

Preparation of Adipic acid from Beef Suet.

Malaguti (*loc. cit.*) states that adipic acid may be easily obtained by heating beef suet with ordinary nitric acid in a flask fitted with a reflux condenser, until the oily layer disappears. The contents of the flask are then concentrated on a water bath until the liquid solidifies on cooling, and the crystals are collected, washed first with nitric acid and then with water, and finally recrystallised from water; the crystals, said to consist of adipic acid, melt at 130°, whereas adipic acid melts at 148—149°. In repeating this experiment, 500 grams of clarified beef suet were treated with about 200 c.c. of fuming nitric acid; the action, which at first was very violent, quickly subsided, and the flask was then heated on a sand bath, nitric acid being added from time to time to replace loss by evaporation; after 32 hours digesting, the oily layer had disappeared. The contents of the flask were evaporated on the water bath to remove the excess of nitric acid, and the viscid residue was dissolved in boiling water; on evaporating the solution to the consistence of a syrup, and leaving it for a week, the whole solidified to a gritty, crystalline mass. This, according to Malaguti, should consist of nearly pure adipic acid, but I found that, after recrystallisation from water, it melted at 109—112°. The acid is readily soluble in ammonia, and is reprecipitated by hydrochloric acid. The silver salt, obtained as a white amorphous precipitate on adding silver nitrate to a neutral solution of the ammonium salt, was analysed.

0·7542 gave 0·4172 AgCl. Ag = 55·14 per cent.

A combustion of the recrystallised acid gave results which agreed neither with the formula of sebacic acid nor with that of adipic acid, and, judging from this and from the ill-defined melting point, it cannot be regarded as a simple acid but must be a mixture of two or more acids. An attempt was made to separate the various constituents by treating the dried and powdered product with successive small quantities of anhydrous ether, and in this way two fractions of definite melting point were isolated. The first ethereal extract, on evaporation, left a white, crystalline residue, which separated in colourless plates on slow evaporation of its alcoholic solution; the crystals melted at 122—129°. The crystalline residue from the second ethereal extract melted at 124—125°, and that from the third and fourth at 127—128°. The first two fractions were too small to deal with. The third and fourth were mixed, dissolved in dilute ammonia, the excess of ammonia driven off, and silver nitrate added; the white, amorphous precipitate which was thrown down gave the following result on analysis.

0·2544 gave 0·1317 Ag. Ag = 51·72 per cent.

The substance is evidently sebacic acid, as this melts at 127—128°, and its silver salt contains 51·92 per cent. of silver.

The residue left after the product had been extracted 10 times successively with ether melted at 100—112°; and on crystallisation from alcohol yielded colourless plates melting at 105—107°. On analysis it gave the following results.

0·1228 gave 0 2581 CO_2 and 0 0937 H_2O. C = 57·32; H = 8·47.

Azelaïc acid, $C_7H_{14}(COOH)_2$, melts at 106°, and contains C = 57·45 and H = 8·51 per cent.

The silver salt gave the following results on analysis.

0·226 gave 0·1216 Ag = 53·8 per cent. of silver.

This acid appears to be azelaic acid.

The action of ordinary nitric acid on beef suet was next tried. 50 grams of purified beef suet were heated on a water bath for 48 hours with 250 c.c. of nitric acid, sp. gr. 1·42, the excess of acid driven off, and the whole evaporated to dryness. The viscid, semi-crystalline residue was boiled with water, in which it nearly all dissolved, and the solution concentrated; on standing for three days, hard, gritty crystals were deposited, which, after recrystallisation from hot water, melted at 95—96°. The amorphous, white silver salt yielded the following result on analysis.

0·372 gave 0·1861 Ag. Ag = 50·2 per cent.

The acid was again carefully recrystallised from water, and analysed.

0·1085 gave 0·2422 CO_2 and 0·0905 H_2O. C = 60·88; H = 9·28.
0·2722 „ 0·6065 „ 0·2312 „ C = 60·78; H = 9·43.

The results are in accord with those which would be furnished by a dibasic acid, $C_{11}H_{20}O_4$; this requires C = 61·1; H = 9·26 per cent.; and its silver salt Ag = 50·7 per cent.

It is evident, from the foregoing results,

1. That the action of nitric acid on beef suet is a complex one.
2. That the products vary with the concentration of the acid used.
3. That sebacic acid and azelaïc acid are amongst the products of the action of fuming nitric acid on beef suet, whilst ordinary nitric acid gives an acid having the formula $C_{11}H_{20}O_4$.
4. That adipic acid is not formed by the oxidation of sebacic acid.

The adipic acid used in the preparation of the derivatives subsequently described was obtained by a modification of V. Meyer's process (*Ber.*, 1887, **19**, 3244, and *Ber.*, 1888, **21**, 24). Glycerol was converted into glyceric acid by slow oxidation with nitric acid, the excess of nitric acid driven off by heating the products on a water bath, and the crude glyceric acid diluted with water until it had a sp. gr. of 1·26. 176 grams of iodine were then gradually added to 100 c.c. of the solution of the crude acid, previously mixed with

22 grams of red phosphorus, and the viscid, brown liquid which remained after the action was over was well cooled; the crystalline scales of β-iodopropionic acid, which separated, were collected on a vacuum filter and recrystallised from carbon bisulphide. The β-iodopropionic acid was converted into adipic acid by heating it with finely-divided copper at 160°.

α-Monobromadipic acid, $COOH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CHBr{\cdot}COOH$.—This acid was obtained by Gal and Gay-Lussac (*Annalen*, 1870, **155**, 250), but not in a pure state. Adipic acid (1 mol.) was heated with bromine (2 mols.) at 160° in a sealed tube for two hours. When cold, the contents of the tube, which consisted of a nearly colourless, crystalline mass, were extracted with anhydrous ether, and the residue left on the evaporation of the ether was recrystallised from absolute alcohol; the colourless crystals obtained melted at 131°.

0 1196 gave 0·7994 AgBr. Br = 35·98.
0 1146 „ 0·1356 CO_2 and 0 0434 H_2O. C = 32·2; H = 4·2.
$C_6H_9O_4Br$ requires C = 32·0; H = 4 0; Br = 35·55 per cent.

α-Hydroxyadipic acid, $COOH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH(OH){\cdot}COOH$.—α-Bromadipic acid was warmed for a few minutes with a dilute solution of potash, acidified with hydrochloric acid, and shaken with ether; the ethereal solution, on evaporation, left a nearly colourless oil, which solidified almost entirely on standing. The crystals, when drained on a porous tile and recrystallised from ether, melted at 151°, and sublimed undecomposed. They are easily soluble in alcohol, ether, and water.

The following results were obtained on analysis.

0·2021 gave 0 3282 CO_2 and 0·0117 H_2O. C = 44·5; H = 6 4.
$C_6H_{10}O_5$ requires C = 44·4; H = 6·1 per cent.

Monobromadipic acid, when heated with water, yields the hydroxy-acid, but the product is contaminated with large quantities of uncrystallisable bye-products, which render its purification difficult.

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XXI.—*On the Determination of High Temperatures by means of Platinum-resistance Pyrometers.*

By C. T. Heycock and F. H. Neville.

In the experiments on alloys (*vide* Trans., 1890 to 1894), the results of which we have hitherto communicated to the Society, we have made use of mercury thermometers, whose fixed points were determined by the platinum-resistance method. As we are now examining alloys which melt at temperatures above the range of the mercury thermometer, it has become necessary for us to select a method of measuring high temperatures. Four methods have been commonly used for this purpose.

(*a*.) Air thermometers.
(*b*.) Calorimetric methods.
(*c*.) The change in the electromotive force of a thermo-couple.
(*d*.) The change in resistance of a platinum wire.

It was necessary, for the purpose of our experiments, to select a method which would not only rapidly indicate the temperature, but would measure small differences of temperature with accuracy. Methods (*a*) and (*b*) were consequently out of the question, and, from the results hitherto published, it appeared that (*c*) was wanting in delicacy. We therefore decided to adopt method (*d*), especially as we already had some acquaintance with it.

The method of platinum-resistance pyrometry, first suggested by Siemens, has been brought to great perfection by Callendar and Griffiths (*Phil. Trans.*, A, 1887, p. 161; A, 1891, p. 119), and the necessary apparatus is now made by the Cambridge Scientific Instrument Company in a very practical form.

The results of this paper were obtained as a necessary preliminary to a study of alloys, which is not yet completed, but which we hope to publish shortly. Our experience leads us to the conclusion that platinum-resistance thermometry is a most valuable method, although it has not yet been much used by chemists. We therefore venture to lay before the Chemical Society a somewhat full account of the work gone through by us in the determination of the temperatures of solidification of certain metals and salts.

Callendar having, so far as we know, only compared the air and platinum thermometers up to 600° C., our results beyond that temperature required confirmation. As will be seen in Section III, that confirmation is largely to be found in the excellent work of Holborn and Wien (*Ann. Phys. Chem.*, 1892, **47**, 107), and of Victor Meyer, Riddle, and Lamb (*Ber.*, 1894, **27**, 3129).

The present paper is divided into the following sections

1. Description of the method and instruments.
2. Study of the behaviour of the pyrometers.
3. Discussion of results and comparison with those of other observers.
4. Determination of the fixed points.

SECTION I.

Description of the Method and Instruments.

In platinum-resistance thermometry, a coil of platinum wire is introduced into the space whose temperature is to be ascertained, and the electrical resistance of this coil is measured. Such a coil, properly protected and mounted, constitutes a platinum-resistance thermometer or pyrometer.

Let R_0, R_{100}, and R_t be the resistance of the wire at the temperatures 0, 100, and t Centigrade. Then, if we assume that the change in temperature is proportional to the change in resistance, the temperature will be given by the expression

$$\frac{R_t - R_0}{R_{100} - R_0} \times 100 \ldots\ldots\ldots\ldots\ldots\ldots (1).$$

A scale of temperatures could thus be formed, having a value similar to that of the mercury in glass scale; for this latter scale is based on the assumption that the change in temperature is proportional to the change in the apparent expansion of mercury.

But the temperature given by expression (1) would, at high temperatures, differ considerably from that of an air thermometer at the same point.

Callendar therefore assigns the name "platinum temperature" to this quantity, and denotes it by the symbol pt. We thus have

$$pt = \frac{R_t - R_0}{R_{100} - R_0} \times 100 \ldots\ldots\ldots\ldots\ldots\ldots (2),$$

and the symbol t is reserved for the temperature that would be given by an air thermometer.

In order to convert temperatures on the platinum scale to those on the air scale, it is necessary to determine the relation between pt and t. Callendar found that, up to about 600° C., the results of his comparisons between the air and platinum thermometers were well represented by the equation

$$t - pt = \delta\{(t/100)^2 - t/100\} \ldots\ldots\ldots\ldots\ldots (3).$$

Here δ is a constant, depending apparently only on the *chemical* composition of the wire used.

R_0 and R_{100} can be found by immersing the instrument in ice and steam in the manner usual with mercury thermometers; we can then get δ by determining R_t, and therefore pt, for some accurately known value of t (see Section IV).

Callendar and Griffiths have, by very thorough experiments with the air thermometer, shown that the boiling point of sulphur under a pressure of 760 mm. of mercury is 444·53° C. (*Phil. Trans*. 1891A, p. 119),* and they recommend that platinum thermometers should be immersed in the vapour of boiling sulphur, and R_s, and thence pt_s, found. Equation (3) will then give δ. This method has been repeatedly applied to all our thermometers. Details as to the sulphur determinations are given in Section IV. The value of δ having been thus ascertained for a particular thermometer, it will be seen from inspection of the tables that it changes little if at all for that thermometer, even after heating to very high temperatures.

We can now tabulate, as in Table I, the values of t in terms of pt, or we can plot $t - pt$ and pt in the manner recommended by Callendar. The curve thus made enables us to deduce the air-thermometer temperatures corresponding to the values of pt found in our experiments.

TABLE I. $\delta = 1{\cdot}50$.

pt.	$t - pt$.	$t°$ C.	pt.	$t - pt$.	$t°$ C.
−100	+2·9	−97·1	600	+54·4	654·4
0	0	0	700	+79·4	779·4
50	−0·4	49·6	800	+110·7	910·7
100	0	100·0	900	+149·4	1049·4
200	+3·1	203·1	1000	+197·0	1197·0
300	+9·8	309·8	1100	+225·0	1355·0
400	+20·2	420·2	1200	+326·7	1526·7
500	+34·9	534·9	1300	+416·0	1716·0

It is evident from Equation (3) that so long as t is constant, $t - pt$ is proportional to δ; hence a table or chart giving $t - pt$ in terms of pt, which has been constructed for a particular value δ of the constant, can be used for another value δ', by multiplying by the factor δ'/δ. In order to form some idea of the relation between t and pt, we give Table I for the case of $\delta = 1{\cdot}50$. An error of one in the second decimal place of δ produces an error of 0·9° in the computation of t at 1000°, and of course the error introduced at lower temperatures is proportionately less.

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* This number is lower by 3·9° than the commonly accepted number due to Regnault (*Mém. de l'Institut*, 26, 1862, p 527), but they give what appears to be a satisfactory explanation of the discrepancy.

The Pyrometer and Wheatstone's Bridge.—As our thermometers were designed for high temperatures, we shall in future always speak of them as *pyrometers*. They were constructed by the Cambridge Scientific Instrument Company, according to the designs of Callendar (*Phil. Mag.*, July, 1891), and have been modified by us in details only. In the type we are now using, the coil is made of the purest platinum wire obtainable, of a diameter varying in different instruments from 0·008 to 0·004 inch. The coil has a resistance of about 3·3 ohms at 0°. The wire is wound double round a frame composed of two narrow rectangular strips of thin mica. These strips are equal, and are set with their planes at right angles, so as to intersect along their longer diameters. The section of the frame is thus a cross, and the coil forms a helix of square section touching the micas at their edges only. The coil itself is (when made of 0·004-in. wire) about 20 mm., and the wire about 200 mm., long. The coil hangs very near the bottom of a porcelain tube, Fig. 1, closed at the lower end, and glazed within and without. This tube is 400 mm. long, 12 mm. in external, and 7 mm. in internal, diameter, and the mica frame slides into it easily. The leads from the ends of the coil are made of stout platinum wire (0·025 in. diameter) to near the top of the tube, where they are soldered to copper wires terminating in binding screws.

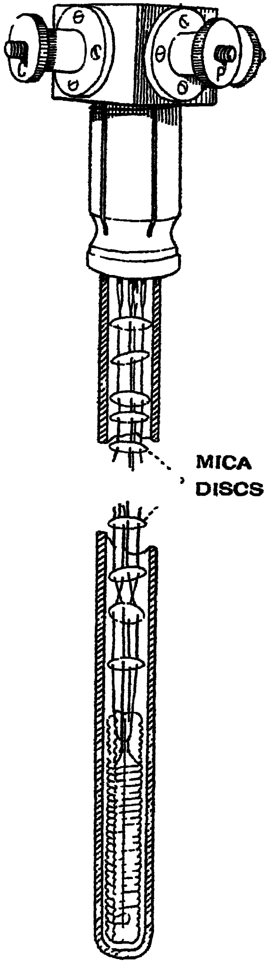


FIG. 1.—General view of the head and interior of a pyrometer.

In order to avoid convection currents, and also to prevent accidental contacts between the leads inside the tube, a number of circular mica discs are threaded on the leads. These discs fit the tubes fairly tightly, and render the wires and coil more rigid.

The coil with its two leads as here

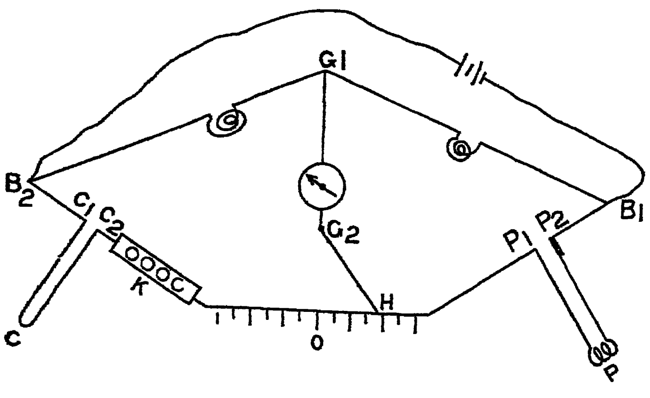
described might be made one arm of a Wheatstone's bridge, and the resistance taken in the usual way, but the disadvantage of this is that we should be measuring not only the varying resistance of the coil, but also that of the leads, parts of which will be at very different temperatures. The errors thus introduced are analogous to those due to the unimmersed part of the stem of a mercury thermometer.

To avoid this difficulty, the arms of the bridge are made equal, and the arm which contains the resistance box also contains a wire running down the tube of the pyrometer to a point just above the top of the coil, and thence back to the bridge. This wire is called the "compensator," and it should have the same resistance as the leads from the coil to the bridge; the compensator is of platinum where the leads are of platinum, and of copper where the leads are of copper. It follows that if corresponding parts of the compensator and of the pyrometer leads are near together so as to be at the *same* temperature, the resistances introduced by them into the arms of the bridge will be equal at *all* temperatures, and, consequently the balance will be independent of the temperatures of these wires.

The resistance of the leads is thus eliminated from our measurements, and we have to deal only with the resistance of the short coil, constituting what by analogy may be termed the bulb of the thermometer.

Between the top of the pyrometer tube and the binding screws of the bridge the compensator and the pyrometer leads form a fourfold insulated cable, which may be of any required length. At each end, a few inches of this cable are unravelled for attachment to the binding screws. The connections are represented diagrammatically in Fig. 2, the lettering being the same as on our apparatus.

FIG. 2.



The arms G_1 B_1 and G_1 B_2 consist of coils of equal resistance, and the arms B_1PH and B_2CKH are made equal by taking out or putting in plugs in the resistance box K, and by shifting the contact piece H on the divided bridge wire. The long leads starting from C_1 C_2 and P_1P_2 form the cable to four binding screws on the head of the pyrometer tube; C and P, though apart in the diagram, are in reality close together at the lower end of the pyrometer tube. The zero of the divided bridge wire should be at O, its middle point, that is to say, if the gaps C_1C_2 and P_1P_2 were filled up by thick, short wires of equal resistance, the bridge should balance at O.

Then if R is the resistance of the pyrometer coil, r that introduced by the resistance box, and S that of the length OH of the bridge wire, we see that

$$R = r + 2S,$$

so that the effective value of a unit length of the bridge wire is twice its real resistance.

The coils of the box are of platinum silver with a temperature coefficient of 0·00027. The resistances are measured in a unit equal to 0·01289 true ohm. The coils form a progression in powers of 2, and are lettered as well as numbered.

Their nominal values are given in line 2 of Table II, and the corrections to be added to these nominal values are given in line 3.

TABLE II.

H.	G.	F.	E.	D.	C.	B.	A.
5	10	20	40	80	160	320	640
+0·105	+0·05	+0·02	−0·16	−0·1	+0·06	−0·20	−0·08

A unit division of the bridge wire is approximately equal to a unit of the coils. Each unit division is divided into 10 equal parts, and, by means of a vernier, tenths of each of these can be read.

A very dead beat reflecting galvanometer should be used. On account of the numerous metallic junctions in the circuit, there may sometimes be considerable thermoelectric effects. These troublesome effects were almost entirely eliminated by the use of Griffiths' thermoelectric key (*Phil. Trans.*, vol. 184 A, 398).

The current from one Leclanché cell running through 100 ohms in the battery circuit is the most suitable. This current produces no apparent heating effect in the coil of the pyrometer, but if a resistance of 20 ohms be substituted for that of 100, the heating effect of the current on the wire of the coil is perceptible, especially at low temperatures (see Pyrometer 8, July 30, 1894). The heating effect shows itself by a creep on the scale of the galvanometer, lasting for some moments after the current has been put on and the first swing has ended.

The preceding statements give the most essential facts about the apparatus as it comes from the makers, but before accurate work can be done with it, the bridge wire must be calibrated and the errors of the coils determined. These are processes involving great care and a good deal of arithmetical work. An intelligible account of the methods we adopted to calibrate the bridge wire and correct the coils would be too lengthy for the present paper; a description of such methods will be found in text-books on practical physics. The result of the calibration of the bridge wire is given in Table III. Column 1 gives the bridge-wire reading, column 2 the correction, always positive, to be added to reduce it to box units.

TABLE III.

B.W. reading	Correction.	B W. reading.	Correction.
−10	0·26	0	0·119
−9	0·246	1	0·114
−8	0·232	2	0·121
−7	0·214	3	0·129
−6	0·193	4	0·128
−5	0·175	5	0·130
−4	0·161	6	0·129
−3	0·148	7	0·115
−2	0·138	8	0·105
−1	0·129	9	0·090

We see from Tables II and III that the corrections to be added to the bridge-wire reading may amount to more than 0·2°, and that the coil corrections are of the same order.

When a pyrometer is first received from the makers, its FI* is generally too great. It is adjusted by removing the tube and slightly shortening the coil by twisting the end. The twisted junction is then fused in a small oxyhydrogen flame; after this, any unfused turns are untwisted and the FI determined. With a little practice, it is easy to adjust the pyrometer so that its FI is correct to within 0·1 per cent. If, in the process of fusing, the coil is shortened too much, it can sometimes be corrected by slightly stretching with a pin, but care must be afterwards taken to anneal the coil before determining its FI. Before making the final determination of the FI, the coil and leads should be annealed by heating the pyrometer, for about two-thirds of its length, to the highest temperature of a tube-combustion furnace. The saving of time in applying corrections is so great with adjusted pyrometers, that a little labour in getting the FI within 1 per cent. of 100 box units is well repaid.

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* The symbol FI denotes Fundamental Interval, that is, $R_{100}-R_0$.

To Record and Reduce an Observation.—The bulb of the pyrometer being immersed in the substance whose temperature is required, a balance is obtained on the bridge, and the following points are noted.

1. The time.
2. The letters of the plugs out of the resistance box.
3. The bridge-wire reading.
4. The temperature of the coils inside the box.
5. The barometer, read to 1/10th mm. (in cases where pressure affects the result).

These are entered in the note-book, of which a sample page is given in Table IV (p. 168).

The next thing is to ascertain the corrections to be added to the observed values. Under the coil letters, we write the total corrected value of the coils in circuit taken from Table II.

Under the bridge-wire reading is placed the calibration correction from Table III. Under the box temperature comes the increased resistance of the coils in circuit due to their excess of temperature above 20°, the temperature for which Table II is correct.

If the experiment is a boiling point, we usually write, as a quantity to be subtracted, the excess of the resistance over what it would have been if the pressure had been 760 mm. We thus reduce the reading to one at normal pressure. With thermometers in which the $R_{100}-R_0$ (or FI) is about 100 and the δ about 1·5, we may assume that the value of R_{100} increases by 0·037, and of R_s increases by 0 072 for each millimetre of barometric pressure above 760, and conversely. For instruments in which the FI differs considerably from 100, or the δ from 1·50, the corrections are somewhat more troublesome (see Section IV).

The numbers under (2) and (3), and the corrections under (3), (4), and (5) are now to be added, and the result is R, the resistance of the pyrometer under the given conditions.

If the fixed points are already known, we can now find

$$pt = \frac{R - R_0}{FI} \times 100$$

where FI is the symbol for $R_{100} - R_0$.

The δ chart then gives us $t - pt$, and, therefore, t, the Centigrade temperature on the air-thermometer scale.

A resistance can generally be read with several different combinations of coils and bridge wire. The results should, of course, be identical; and in practice, the groups of values of R_0, R_{100}, and R_s got thus, do not usually differ by more than 0·02° from one another, and are generally much nearer. In the sample page, such groups of readings are given, but in the more condensed tables each R_0, R_{100}, or R_s is itself the mean of such a group; the separate readings agreeing so well that it would be waste of space to give them.

TABLE IV.—*Pyrometer* 14.

	Time. 1.	Coils. 2.	Bridge wire. 3.	Box temp. 4.	Barometer. 5.	R.	
1894. Dec. 21 B. p. of S.	5·51	AEG 689·81	−7·022 +0·215	21·04° +0·191	759·86 +0·010	683·204	
,,	5·55	AE 679·76	+3·103 +0·129	21·05 +0·193	759·84 +0·012	683·202	
,,	5·59	AEH 684·865	−2·007 +0·139	21·08 +0·198	759·84 +0·012	683·207	
,,	6·4	AFGH 675·095	+7·798 +0·108	21·1 +0·202	759·84 +0·012	683·215	
						683·207	Mean R_s.
Ice	6·40	CDF 259·98	+1·778 +0·119	21·01 +0·071	..	261·948	
,,	6·45	CDFH 265·085	−3·368 +0·153	21·01 +0·071	..	261·921	
						261·935	Mean R_0.
Steam	6·55	BE 359·64	+2·008 +0·120	21·06 +0·104	759·05 +0·035	361·907	
,,	7·0	BEH 364·745	−3·138 +0·150	21·06 +0·104	759·00 +0·037	361·898	
,,	7·5	BEG 369·69	−8·152 +0·234	21·10 +0·107	758·95 +0·039	361·918	
						361·908	Mean R_{100}.
Dec. 31 Ice	5·40	CDF	+1·938	20·0	..	262·037	FI = 99·97
,,	5·45	CDFH	−3·225	20·0	..	262·010	$\delta = 1·511$
						262·024	Mean R_0.
Gold 1,200 gr.	6·5	ABCEH	+4·80	20·25	..	1169·73	F. p. of Au is 1062·0° C.
	6·10	,,	+4·79	,,	..	1169·73	
	6·15	ABCEG	−0·185	20·40	..	1169·73	

The third decimal place in the constants has, of course, no claim to accuracy, but, as the observed readings of R_0 and R_{100} with different coils often agree to within 0·005, we think that accuracy in the second figure is gained by giving the third.

The separate readings of R_0 given in Table IV do not agree quite as well as usual, and the sulphur readings agree more closely than is usual. The small discrepancy between the ice points of December 21 and December 31 is probably due to the pyrometer having been disconnected from the leads to the box in the interval. It does not affect the FI.

SECTION II.

As one of the most important questions about platinum pyrometers is that of the constancy of their zero, fundamental interval, and δ, after exposure to high temperatures, we have tabulated in strictly chronological order the experiments made with certain pyrometers (see Tables V to IX, pp. 170—183).

In the tables, column 1 gives the date of the experiment, 2 the hour or duration, 3 specifies the nature of the experiment, 4 symbolises the experiment, and the sub-index is the ordinal number for that species of experiment. Thus Al_3 means the third experiment on aluminium with the particular pyrometer.

Column 4 is useful for quickly finding an experiment.

Column 5, headed $R°_{100}$, gives the values of the steam and ice points found on certain dates. Opposite them, in column 6, is the index number for referring to these constants; and in column 7 is the FI or $R_{100}-R_0$. Thus the three columns 5, 6, 7, read vertically, record the changes in the constants of the pyrometer due to the treatment it has undergone.

Column 8 gives the resistance observed during the experiments referred to in 3 and 4. Column 9 gives the corresponding *pt*, and the suffix refers to column 6, and indicates the constants used in calculating *pt*. In cases where there is no suffix, the constants immediately preceding have been used.

Column 10 gives the Centigrade temperature calculated from equation (3), or taken from a chart.

On the Changes in the Constants of the Pyrometers.

By studying the columns enclosed between the thick vertical lines in the tables, we can trace the gradual change in the constants due to the treatment to which the instrument has been subjected. The change in FI is the most important.

Consider Pyrometer 7. Here, with one trifling exception, the FI rises

TABLE V.—*Pyrometer 7.*

Dat	Time.	Nature of Experiment.		R°_{100}.	Index No.	FI.	R.	*pt.*	δ = 1·500. *t.*
July 2	..	.. ..	Steam	358·43	1	99·92			
,, 2	..	.. ..	Ice	258 51					
,, 3	..	.. ..	Steam	358·385	2	99·898			
,, 3	..	.. ..	Ice	258·487					
,, 3	..	Some hours at a red heat.							
,, 4	3 hours	F. p. of 68 grams aluminium............	Al_1	..	..	..	859·21	601·49 (3)	656·2
,, 5	,,	,, 282 ,, ,, ...	Al_2	..	..	..	857·71	599·96 (3)	651 4
,, 6	..	.. ..	Steam	358·40	3	99·87			
,, 6	..	.. ..	Ice	258·53					
,, 8	..	B. p. of sulphur (early method)..........	S_1	..	..	..	679·39	421·41	∴ δ = 1·510*
,, 15	..	.. ..	Steam	358·176	4	99·968			
,, 15	..	.. ..	Ice	258·508	5	100·002			
,, 16	..	.. ..	Steam	358·51					
,, 16	..	Extracted coil from tube and dried	,,	358·58	6	100 0			
,, 16	..	.. ..	Ice	258·53					
,, 16	1 hour	Heated to bright redness, then	,,	258·546					
,, 29	2 hours	F. p. of 700 grams copper in clay crucible	Cu_1	..	..	..	1177·8		†
,, 29	,,	,, 500 ,, ,, plumbago do.	Cu_2	..	..	..	1179 5		‡
,, 29	..	.. ..	,,	..	..	..	1179·4	920 9	1079·5
,, 29	..	.. ..	,,	..	..	..	1180·0		§
,, 29	..	Added 100 grams copper	,,	..	..	..	1180·4		
,, 29	..	.. ..	,,	..	..	..	1180·3	921·8 (6)	1080 9§
,, 29	..	.. ..	,,	..	..	..	1180·3	921·8 (7)	1090 9
,, 29	..	Added 64 grams copper	,,	..	..	..	1180·4	..	1081 0
,, 29	..	.. ..	Ice	258·02					
ug. 1	..	.. ..	,,	258·04	7	100·05			
, 1	..	.. ..	Steam	358·09					

6		Changed to a new tube. Mica plate of coil was found to be broken.	Ice	258·15	8	100·08			
6			Steam	358·23					
6		B p. of sulphur after 2 hours' immersion	S_2	..	..	..	680·06	421·58	
7		F. p. of 300 grams antimony	Sb_1	..	..	..	834·53 834·33	575·2 (9)	624
8		..	Ice	258·136	9	100·192			
			Steam	358·328					
„ 8		F. o[illegible] grams antimony in sala- und[illegible] ucible.	Sb_2	..	..	..	833·8	574·5 (9)	623
„ 8			„		..	..	833·7		
1895. Jan. 9		..	Ice	258·269	10	100·142			
			Steam	358·411					
9		F. p. of 500 grams pure antimony from tartar emetic	Sb_3	..	..	..	838·50	579·41	629
	1	.. ..	„	..	..	..	838·50		
	1	.. ..	„	..	..	..	838·45	579·36	629
	1	.. ..	„	..	..	..	838·52		
	6	„ „ „	Sb_1	..	..	..	838 53		
	6	„ „ „	„	..	..	..	838·54	579·45	629

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* The form of screen used to protect the pyrometer against radiation and drip of condensed sulphur was afterwards abandoned for a better one—the perforated protector. (See Sec. IV.)

† The copper had become somewhat oxidised by melting without a flux, but during the determination its surface was as usual protected by a layer of molten borax, which, when cold, was found to be deep green.

‡ In this series, there was probably no oxidation, as the borax remained colourless.

§ Surfusion was shown by a slight rise of temperature at the moment of freezing.

|| Well marked surfusion.

¶ Surfusion of many degrees.

** Much surfusion.

TABLE VI.—*Pyrometer* 8.

Date.	Time.	ure of Experiment.		R°_{100}.	Index No.	Fl.	R.	*pt.*	δ − 1·501. *t.*
1894. July 2	..	..	Steam	359·506	1	100·171			
" 2	..	.. ..	Ice	259 332					
" 5	..	F. p. of 282 grams aluminium	Al_1	..	..	..	860·38	600	654·5
" 5	..	.. ..	"	..	..	..	860·86	600·18	654·8
" 6	..	.. ..	Ice	259·531	2	100·166			
" 6	..	.. ..	Steam	359·700					
" 9	..	B. p. of sulphur (early method)	S_1	..	..	..	681·52	421·29	∴ δ = 1·517
" 10	..	F. p. of 805 grams copper (best commercial bar and rod)	Cu_1	..	..	..	1181·46	920·1 (2)	1079 2
" 10	..		"	..	..	..	1181·30	920 2 (2)	1079·0
" 10	..	" " "	"	..	..	..	1181·30	921·1 (3)	1080 7
" 11	..	B p of sulphur (early method)	S_2	..	..	..	680 58	421·15 (3)	∴ δ = 1 507
" 11	..	F. p. of same pot of copper as on July 10	Cu_2	..	..	..	1181 29	921·3 (3)	1080 5
" 11	..	.. ..	"	..	..	..	1181 18		
" 12	..	Tube contaminated with borax	Steam	359·36	*				
		Cleansed from adhering borax	"	358·62	3	100·16			
" 12	..	.. ..	Ice	258·46					
" 12	..	F. p. of 700 grams zinc	Zn_1	..	..	..	658·34	399·22 (3)	419·35
		" "	"	..	..	..	658·31		
" 12 " 13	..	Heated in molten zinc for many hours							
" 15	..	..	Ice	258·437	4	100·185			
			Steam	358·622					

„ „	29 30	1 hour	In changing tube, the end of the coil was broken. Coil was mended and annealed at red heat. 100 ohms as usual in battery circuit	Ice Steam	257·69 357·59	5	99·9			
			20 ohms in battery circuit.............	Ice Steam	257·835 357·680	6	99·815			†
Aug.	1	2 hours	F. p. of 300 grams silver (cooled in air) ..	Ag_1	..		..	1087·71		
			„ „ (cooled in coal gas)........	„	..		..	1091·93		
			„ „ „	„	..		..	1091 91	835·05 (5)	958 8
			„ „ „	„	..		..	1091·90		
„	2	..	.. ..	Steam	357·510					
„	2	..	.. ..	Ice	257·575		99 935			
„	6	..	Heated in sulphur vapour.							
„	15	..	B. p of sulphur. Perforated protector..	S_8	..		..	678·80	421·50	∴ δ = 1·504‡
„	15	..	.. ..	Steam	357·50		99·94			
„	15	..	.. ..	Ice	257·56					
„	16	..	F. p. of 268 grams silver. No stir	Ag_2	..		..	1091·0	833·94 (8) 834·0 (9)	957·3§
„	17	..	.. ..	Ice	257·46					
„	17	..	Added 30 grams silver to above.........	Ag_3	..		..	1091·7	834·7 (8)	958·3
„	17	..	.. ..	Ice	257·46					
„	19	..	F. p of aluminium. No flux. Automatic stirring	Al_2	..		..	857·64	600·4 (10)	655·1
			Same Al. No flux. No stir............	Al_3	..		..	856·35		
„	20	..	.. ..	Steam	357·37		99·96			
				Ice	257·41					

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* The greatest care is needed in cleaning off any flux from the outside of the tube before determining R_{100} and R_0, otherwise R_{100} is too high and R_0 too low.

† The heating effect of the current was well marked in ice, and it was necessary to pass the current through the coil for several minutes before a steady temperature was attained.

‡ This series of boiling points was carried out with the improved "perforated protector," described in Section IV. The separate readings were almost identical. We therefore use this value of δ.

§ Perhaps insufficient immersion.

TABLE VI—*continued.*

Date.	Time.	Nature of Experiment.		R°_{100}.	Index No.	Fl.	R.	*pt.*	$\delta = 1 \cdot 501$. *t.*
1891.									
Sept 30	..	.. ..	Ice	257·436	11	99·965			
			Steam	357·401					
" 30	6 hours	At 700° C.							
Oct. 1	12 hours	F. p. of 175 grams aluminium. Flux....	Al_4	..	..	..	857·20	599·9 (12)	651·5
" 2	..	.. ..	Ice	257·13	12	99·99			
			Steam	357·42					
" 3	12 hours	F. p. of 400 grams zinc (in a reducing atmosphere of coal gas)............	Zn_3	..	..	..	655·9	398·53	118·57
			"	..	..	..	655 91		
" 7	..	Tube, much corroded, let water through. Dried pyrometer. New tube.........	Ice	257 59	13	99·96			
			Steam	357 55					
" 8	..	F. p of 189 grams aluminium. It was believed to be Schaffhausen. No flux. Four identical readings...............	Al_5	..	..	..	855·2	598·0	652·2
" 9	..	F p. of 211 grams of same Al	Al_6	..	..	..	855·4	598·2	652·1*
" 15	..	Pyrometer broken.							

* We have reason to think that this aluminium was not so pure as the aluminium used in the other experiments.

TABLE VII.—*Pyrometer* 11.

Date.	Time.	Nature of Experiment.		R°_{100}.	Index No.	Fl.	R.	*pt.*	$\delta = 1\cdot497$. t.
1891.	1 hour	Annealed at a red heat.							
July 14	..	B. p. of sulphur (early method)	S_1	..	..	..	683·402	421·11 (2)	∴ $\delta = 1\cdot51$
,, 14	..	.. ..	Ice	259·793	1	100·502			
,, 14	..	.. ..	Steam	360·295					
,, 15	..	.. ..	Steam	360·331	2	100·514			
			Ice	259·817					
,, 29	..	F. p. of 664 grams electrolytic copper..	Cu_1	..	..	..	1187·31		
			,,	..	..	..	1187·10	922·5 (2)	1081·5
			,,	..	..	..	1187·12	921·9 (3)	1080·7
			,,	..	..	..	1186·94		
,, 29	..	.. ..	Ice	259·895	3	100·58			
Aug. 1	..	.. ..	Steam	360·447					
,, 1	..	.. ..	Ice	259·868					
,, 2	2 hours	F. p. of 300 grams silver	Ag_1	..	..	..	1100·08		
,, 2	..	.. ..	,,	..	..	..	1100·14	835·40	958·7
,, 2	..	.. ..	,,	..	..	..	1100·13		
,, 3	..	.. ..	Ice	259·829					
,, 13	..	B. p. of sulphur. Perforated protector	S_2	..	..	..	684·003	421·602 (4)	∴ $\delta = 1\cdot197$*
,, 13	..	.. ..	Ice	259·87	4	100·597			
			Steam	360·467					
Dec. 26	5.30	F. p. of 700 grams Stas' silver	Ag_2	..	..	..	1102·4		
,, 26	5.41	.. ..	,,	..	..	..	1102·42		
,, 26	5.47	.. ..	,,	..	..	..	1102·41	837·5 (4)	961·6†
,, 26	5.55	.. ..	,,	..	..	..	1102·43	836·4 (5)	
,, 26	6.15	.. ..	Steam	360·572	5	100·732			
,, 26	..	.. ..	Ice	259·84					

* The only trustworthy determinations.

† We had specially purified this silver by Stas' method of precipitation with ammoniacal cuprous sulphite.

TABLE VIII.—*Pyrometer* 13.

Date.	Time.	Nature of Experiment.		R°_{100}	Index No.	FI.	R.	*pt.*	δ = 1·500. *t.*
1894.		Annealed at a red heat.							
Aug 3	..	F. p. of 300 grams silver (no record of use of reducing gas during cooling)	Ag_1	..	..	..	1100·8		
			"	..	..	..	1100·8		
			"	..	..	..	1100·8	833·2 (1)	955·9
" 4	..	.. ..	Ice	262·18	1	100·64			
			Steam	362·82					
" 5	..	Heated in sulphur.							
" 5	..	" in molten silver.							
" 5	..	.. ..	Ice	262·22	2	100·69			
" 5	..	.. ..	Steam	362·91					
" 5	..	F. p. of 268 grams silver............	Ag_2	..	..	..	1102·3		
			"	..	..	..	1102·5	831·18	957·7
			"	..	..	..	1102·7		
" 7	3 hours	B. p. of sulphur (early method).	S_1	..	..	..	686·51	421·36	· $\delta = 1·513$
" 7	..	.. ..	Ice	262·331	3	100·665			
			Steam	362·996					
		Stem wholly immersed in steam......	"	362·989					
		Coil end only " "	"	362·986					
" 9	..	B. p. of sulphur, 9" immersion.......	S_2	..	..	..	686·52	421·37	$\therefore \delta = 1·51$
" 10	..	" " stem wholly immersed	S_3	..	..	..	686·68	421·53	$\therefore \delta = 1·502$
" 10	..	" " perforated protector	S_4	..	..	..	686·83	421·68	$\therefore \delta = 1·492$*
" 11	..	" , " " resistance box 20°	S_5	..	..	..	686·78		
		B. p. of sulphur, perforated protector resistance box 30°................	S_6	..	..	..	686·82†		
" 12	..	.. ..	Ice	262·283					
" 12	..	Connections of pyro. and box cleaned	"	262·271	4	(100·67)‡			
" 12	..	.. ..	S_7	..	..	..	686·83	421·71	$\therefore \delta = 1·49$

12	9.55	F. p. of 208 grams silver (sample of Aug. 5)	Ag_{8}	..	..	..	1102·8		
	10.15	.. ..	..	..	.	.. .	1103·0	834·8 (5)	
	10.30	.. ..	..	..	..	..	1103·0	835·1 (4)	958·5
12	..	.. ..	Ice	262·36	5	(100·70) ‡			
17	..	F. p. of 200 grams aluminium. No flux	Al_1	..	..	..	865·2	598·4	652·4
		Automatic rotary stir................	,,	..	..	..	865·0		
17	..	New tube on pyrometer..............	Ice	262·474	6	100·733			
			Steam	363·207					
18	..	F. p. of 182 grams aluminium. Flux. Automatic stir..........................	Al_2	..	..	..	866·4	599·7	654·1
		F. p. of 182 grams aluminium. Flux. Hand stir..........................	,,	..	..	..	866·7		
18 ,, 19	12 hours	In molten aluminium.							
Sept. 20	..	.. ..	Ice	262·45	7	100·78			
,, 20	..	.. ..	Steam	363·23					
,, 20	..	F. p. of 200 grams aluminium	Al_3	..	..	..	867·0	599·8	654·2
,, 23	3 days	In molten aluminium, then..........	Ice	262·448	8	100·806			
,, 23	..	.. ..	Steam	363·254					
,, 24	..	F. p. of 180 grams aluminium.......	Al_4	..	..	..	867·6	600·5	655
,, 24	..	.. ..	,,	..	..	..	868·0		
,, 25	6 hours	In aluminium, then	Steam	363·306	9	100·819			
			Ice	262·487					
,, 25	..	F. p. of 175 grams aluminium	Al_5	..	..	..	867·8	600·5	655
,, 26	6 hours	In aluminium, then	Steam	363·294	10	100·812			
,, 26	..	.. ..	Ice	262·482					
,, 26	..	F. p. of 175 grams aluminium	Al_6	..	..	..	867·8	600·4	654·9
,, 27	6 hours	In aluminium, then.................	Steam	363·366	11	100·83			
,, 27	..	.. ..	Ice	262·536					
,, 27	..	F. p. of 175 grams aluminium	Al_7	..	..	..	867·3	599·7	654·1

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* In this series, changes in the length of stem immersed did not affect the reading.
† These experiments were made to test the temperature coefficient of the box.
‡ These values of FI are interpolations, not observed numbers.

TABLE VIII—*continued.*

Date.	Time.	Nature of Experiment.		R°_{100}.	Index No.	FI.	R.	*pt.*	$\delta = 1 \cdot 500.$ *t.*
1894.									
Sept. 27	5 hours	In aluminium, then	Steam	363·418	12	100·816			
			Ice	262·572					
" 28	..	.. ..	"	262·56	13	100·810			
" 28	..	.. ..	Steam	363·100					
" 29	..	F. p. of 175 grams aluminium.........	Al_8	..	..	..	867·2	599·5	653·9
Dec. 9	..	New tube and f. p. of 145 grams K_2SO_4	K_2SO_4 (1)	..	..	..	1178·6		
" 10	..	New tube.........................	Steam	363·767	14	100·937	1176·0	905·7 (13)	1058·6
" 10	..	.. ..	Ice	262·830					
" 10	..	F. p. of 160 grams K_2SO_4...........	K_2SO_4 (2)	..	..	..	1180·6		
							1180·6	909·2	1062·7
							1180·1		
" 11	..	New porcelain tube..................	Ice	263·83	15	100·90			
			Steam	364·23	16	100·92			
			Ice	263·81					
		In new platinum outer tube	Steam	364·19	17	100·88			
			Ice	263·31					
" 11	3.5	F. p. of 512 grams Na_2SO_4..........	Na_2SO_4(1)	..	..	..	1049·43		
	3.30	.. ..	"	..	..	..	1049·69		
	3.55	.. ..	"	..	..	..	1049·63	779·1	883·2
" 12	..	Heated in molten Na_2SO_4.							
" 13	4 P.M.	F. p. of about 150 grams Na_2CO_3....	Na_2CO_3(1)	..	..	..	1023·96	753·96	849·4*
" 13	4.45	.. ..	"	..	..	..	1023·45	753·45	848·8
" 13	5.20	.. ..	"	..	..	..	1022·75	752·75	847·0†
" 13	..	New porcelain tube	Ice	263·465	18	100·945			
			Steam	364·410					
" 16	12.45	F. p. of 71 grams Patricroft magnesium........................	Mg_1	..	..	..	851·3	582·2	632·8‡
" 16	1.10	.. ..	"	..	..	..	851·3		

,, 16	..	New tube, connections cleaned.......	Ice	263·39	19	(100·95)§			
,, 16	4.10	F. p. of 69 grams Patricroft magnesium (protected surface by a current of dry hydrogen gas). No stir possible	Mg_2	..	..	..	850·7		
	4.30		,,	..	..	..	851·0	582·0	632·5‡
	4.50		,,	..	..	..	851·1		
,, 17	..	Pyrometer, when cold, was found with tube broken and some MgO on leads. Transferred to new tube and heated to 1000°	Ice Steam	263·766 364·732	20	100·97			
,, 17	4.30	F. p. of 300 grams antimony. No stir. Cooled in a current of hydrogen....	Sb_1	..	..	..	813·7	574·3	623·2‖
			,,	..	..	..	814·2	574·8	623·8
,, 18	..	F. p. of 800 grams of tin in hydrogen	Sn_1	..	..	..	493·27	227·27	231·91
			,,	..	..	..	493·36	227·36	
			,,	..	..	..	493·29		
,, 18	..	.. ..	Ice Steam	263·772 364·762	21	100·99			
,, 19	..	.. ..	,, Ice	364·770 263·767	22	101·003			
,, 19	4	F. p. of 577 grams K_2SO_4	K_2SO_4(3)	..	..	..	1184·7	911·7	1066·2
	6	.. ..	..	..	..	..	1181·6	..	1066·1
,, 20	..	On removing pyrometer from tube which had been used for K_2SO_4, the wire stuck to the bottom, and became unwound. It was rewound and heated to 1000°, then	Ice Steam	264·527 365·074	23	101·147			
,, 21	..	B. p. of sulphur	S_8	..	..	..	690·92	421·55	∴ $\delta = 1·500$
,, 24	11.10	F. p. of 782 grams gold.............	Au_1	..	..	..	1183·55	908·60	1061·8

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* Pure $NaHCO_3$, from Brunner and Mond, was used, and heated to 1000° before f. p. was taken.

† A degree below this the whole mass was solid.

‡ Much oxidation of metal during the fusion. Tube much corroded.

§ These values of Fl are interpolations, not observed numbers.

‖ Surfusion of at least 5°.

TABLE VIII—*continued.*

Date.	Time.	Nature of Experiment.		R°_{100}.	Index No.	FI.	R.	*pt.*	$\delta = 1·500.$ *t.*
1894.		Annealed at a red heat.							
	12 5	.. ..	Au_1	..	..	..	1183·61	908·06	1061·9
	12.25	.. ..	,,	..	..	..	1183·65	908·68	1061·9
Dec. 24	12.50	.. ..	Steam	365·986	24	101·205			
			Ice	264·781					
,, 25	..	B. p. of sulphur	S_9	..	..	..	..	..	∴ $\delta = 1·501$
,, 26	..	F. p. of 700 grams silver (Stas)	Ag_1	..	..	..	1110·52		
,, 26	..	.. ..	..	..	..	..	1110·62	835·76	959·5
,, 26	..	.. ..	..	..	..	..	1110·58		
,, 26	..	.. ..	..	..	..	..	1110·66		
,, 26	..	.. ..	Ice	265·785	25	101·573			
			Steam	367·858					
		On removal from tube, the coil stuck and became unwound. We therefore think that on cooling from silver a strain may account for change in the constants.							

regularly and slowly from 99·92 to 100·19, while R_0 decreases by a few tenths of a degree. These changes are the result of at least two heatings to over 1100° for two hours each, and quite half-a-dozen exposures to a bright red heat for many hours, not to speak of many minor heatings and coolings. If these changes had been altogether ignored, the maximum error introduced at 1000° would have been 3° —a quantity of very little importance in the present state of our knowledge of high temperatures.

Pyrometer 8, from July 2 to July 29, when it was broken, tells the same tale; two heatings to over 1100° and several minor heatings altered the FI by only 0·011° and R_0 by 0·9°. From July 29 to October 7, its FI did not vary by more than 0·1°, or its R_0 by more than 0·3°, although it was heated to 1000° on three separate occasions, and to a red heat half-a-dozen times.

Pyrometer 11 tells the same tale of a very slight and gradual increase in the FI in consequence of exposure to temperatures near 1000°.

Pyrometer 13 affords an excellent example of this slow secular rise in the FI; even heating in molten aluminium produces a minute but steady rise.

This appears to be the normal change in pyrometers such as ours. We are disposed to think that the change takes place, not while the coil is hot, but when it cools, and that it is due to the thickening of the mica plates on which the wire is wound. If the micas are examined after prolonged exposure to high temperature, they are found to have become opaque and brittle, and when looked at edgeways they are clearly thicker than at first. Now, the coil on being heated will expand, and the permanent thickening of the mica, which is taking place at the same time, will not cause any strain in the wire; but, as the coil cools, it will contract on to the now larger frame, become strained, and its resistance will increase.

We therefore think that the constants should be determined *before* every important temperature experiment, and providing the leads were well annealed originally, these constants should be used in calculating the *pt*, no matter what the constants may be after the experiments. Unfortunately, we did not come to this conclusion until a late date, so that in many cases constants determined just before the experiment are lacking, and a slight uncertainty is thereby introduced into the results. But the correction is a small one. In some cases we have calculated the results with constants determined both before and after the experiment to show the amount of discrepancy.

Other changes occur in the constants. If the pyrometer is unscrewed from the leads, slight changes in R_0 and R_{100}, due to dirt on

TABLE IX.—*Pyrometer 16. New Sample of Wire.*

Date.	Time.	Nature of Experiment.		R°_{100}.	Index No.	FI.	R.	*pt.*	δ = 1·534. *t.*
1894. Dec. 10	1 hour	Two-thirds of tube containing coil and leads was heated to 800°. Later, the coil was heated to 1000°.							
„ 19	2.10	F. p. of 577 grams K_2SO_4	K_2SO_4 (1)	..	..	..	1228·8		
„ 19	3.10	.. ..	..	..	..	..	1228·9		
„ 19	5.0	.. ..	..	..	..	..	1228·8	900·6 (1)	1066·7
							1228·7		
„ 19	..	In new porcelain tube	Steam Ice	391·784 288·317	1	103·387			
„ 21	..	B. p. of sulphur. Perforated protector ..	S_1	..	..	..	723·610	421·02	∴ δ = 1·534
„ 22	3.25	F. p. of already fused Na_2CO_3..........	Na_2CO_3 (1)	..	..	..	1063·1	710·3	815·3*
„ 22	6.15	F. p. of fresh Na_2CO_3.................	„ (2)	..	..	..	1068·0	751·1	851·7†
„ 22	6 36	.. ..	„	..	..	..	1067·35	753·5	851·1
„ 22	7.0	.. ..	„	..	..	..	1067·27	753·4	851·0
„ 24	2.35	F. p. of 782 grams gold	Au_1‡	..	..	..	1227·29	906·74 (2)	1062·3
„ 24	3.0	.. ..	..	..	..	..	1227·20	906·65 (2)	1062·2
„ 24	3.16	.. ..	..	..	..	..	1227·12	906·56 (2)	1062·1
„ 24	3.35	.. ..	Steam Ice	391·582 287·091	2	103·591			
„ 25	..	B. p. of sulphur. Bar. 774 mm. R is not corrected for bar., but *pt* and *t* are corrected	S_2	..	..	..	725·220	421·061	∴ δ = 1·532
„ 26	4.25	F. p. of 700 grams Stas' silver	Ag_1	..	..	..	1152·93		
„ 26	4.41	.. ..	„	..	..	..	1152·89	834·92	960·9
„ 26	4 50	.. ..	„	..	..	..	1152·86		
„ 26	8.50	.. ..	Steam Ice	391·604 288·013	3	103·591			
„ 27	1.30	F. p. of 700 grams silver (later sample, J. and M.)	Ag_3	..	..	..	1152·68		

„	27	1.40	.. ..	..	..	..	..	1152·91	834·9	960·9
„	27	2.5	.. ..	..	..	..	..	1152·98		
„	27	2 20	.. ..	..	..	..	..	1152·96		
„	27	2.50	F. p. of 298 grams Ag, used Aug. 5 and 17	Ag_3	..	..	..	1152·01	834·0	959 6
„	27	3.5	.. ..	..	..	..	..	1152·03		
„	27	3.58	F. p. of 284 grams silver (later sample, J. and M.)	Ag_4	..	..	..	1152·51	834·6	960·5
„	27	4.10	.. ..	..	..	..	..	1152·72		
„	27	4 20	.. ..	..	..	..	..	1152·54		
„	27	4.37	.. ..	Ice Steam	287·668 391·300	4	103·632			
„	28	12.10	M. p. of K_2SO_4 (V. Meyer's method).....	K_2SO_4 (2)	..	..	..	1242·81	921·6	1083·9
								1243·93	922·7	1085·5
								1243·15	921·9	1084·3
								1242·35	921·1	1083·2
„	28	6 50	M. p. of Na_2SO_4 (V. Meyer's method)....	Na_2SO_4 (1)	..	..	..	1108·15	791·8	902·0
„	28	7.5	.. ..	..	..	..	..	1108·05	791·6	901·8
„	28	7.35	.. ..	..	..	..	..	1108·18	791·8	902·0
„	28	7.50	.. ..	..	..	..	..	1107·93	791·5	901·7
			After the above, the coil proved to have stuck to tube, but some days later it became free.							
1895. Jan.	9	..	.. ..	Ice Steam	288·818 393·010	5	104·162§			
			F. p. of 500 grams pure antimony from tartar emetic (see Pyrometer 7_d)	Sb_1	..	..	..	891·77	578·83	629·75
								891·79	578·85	629·77
								891 88	578·94	629·86

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* This sample of Na_2CO_3 had already been fused for an hour or more, and its f. p. taken with Pyrometer 17. It was falling steadily.

† Platinum protector used to protect the fused salts from impurities. The fused salt was quite clear at 6.15, but became opaque during the later fusing. See Pyrometer 18.

‡ In the calculation of t, the value 1·532 of Dec. 25th is assumed for δ.

§ These considerable changes are no doubt due to strain.

the binding screws, may appear the next time the instrument is used, but the FI is not affected.

If the leads have not been sufficiently annealed in a combustion furnace, irregular changes of several degrees may occur the first few times the pyrometer is used at a high temperature.

Finally, there is a destructive change to which the pyrometers are liable at temperatures above 1000°. This is due to the melting of the glaze on the inside of the porcelain tube. The glaze at present used becomes sticky at 1100°, and melts at a somewhat higher temperature. If the frame, and especially the wire of the coil, does not touch the inside of the tube, the melting of the glaze is probably harmless. But if the wire, or even the mica, touches the fused glaze, it becomes attached to the tube, and, on cooling, a strain is produced. This may only produce an irregular alteration of the constants, and we have used successfully pyrometers in which the coil was fused to the tube. But if the glaze gets on the wire, it probably deteriorates it, and the instrument is no longer trustworthy, even its δ altering. For temperatures above 1100°, it will be desirable to use tubes with no glaze on the inside.

On Pyrometers with Different Values of δ.

Our earlier pyrometers were made of a wire that we knew to have a δ very near 1·50, and we were content at first with a somewhat rough verification of this fact for each pyrometer in turn. But, as we began to realise the accuracy of measurement possible with the pyrometers, it became worth while to find δ with the greatest care, and the later determinations of δ are those we use in calculating *t*. We think that in the determinations of December, 1894, the value of δ is correct to about $\frac{1}{1000}$th part.

It seemed desirable also not to confine our experiments to wire with a δ of 1·50, but to see how far consistent results could be obtained with wire having a different δ.

Table XII of the freezing point of gold throws some light on this question. There we see values of δ varying from 1·50 to 1·58, giving different values of *pt*. but the same values of *t*. Pyrometer 15 had an extraordinary δ of 2·04; but still it gave, at first, the correct freezing point of gold. Similarly, Pyrometer 17, with a δ of 2·1, gave a good freezing point for sodium carbonate. These two pyrometers, however, rapidly deteriorated, and we cannot regard them as absolutely proving that the δ formula is applicable to such an extreme case.

SECTION III.

The Freezing Points of the Metals.

The metals were usually fused in cylindrical crucibles 42 mm. wide and 105 mm. high, made either of plumbago or salamander, or of a fine, close-grained clay. When very slow cooling was required, these cylinders were placed inside another crucible, the interval between the two being filled with pieces of broken crucible. The silver, copper, and gold were fused in an ordinary Fletcher's blast furnace, whilst for the aluminium, magnesium, zinc, tin, and antimony it was sufficient to use a draught furnace. The stirring was effected by hand, except in a few experiments with aluminium, when a rotary stirrer was used. The pyrometers were heated in a muffle furnace before being put into the fused metals, and when the experiment was completed they were transferred to the muffle and allowed to cool. In this way, the life of the porcelain tubes was greatly prolonged. In order to protect the fused metals from absorption of oxygen, we passed either a current of coal gas or of hydrogen over the surface. This precaution was adopted in the cases of tin, zinc, antimony, magnesium, and silver.

Freezing Point of Tin.

Pyrometer 13 gave with 800 grams of tin a freezing point of 231·91°. The tin used was a particularly well crystallised sample; it was free from copper, but contained a trace of iron.

Freezing Point of Zinc.

Pyrometer 8 gave with 700 grams of the metal a freezing point of 419·35°, whilst the same pyrometer gave with 400 grams of zinc the number 418·57°. The zinc used was the purest distilled metal obtainable. The hydrogen produced from the solution of 50 grams, when slowly passed through a red-hot tube, did not deposit the least trace of arsenic or antimony. The zinc contained, however, a small trace of lead and a minute trace of iron, but the quantities were so small that they could only be estimated colorimetrically; no trace of cadmium could be detected.

The discrepancy between our numbers and those of Griffiths (417·6°) is probably accounted for by the fact that he fused his zinc in an iron crucible; this crucible was afterwards found to have been considerably attacked.

As our object was to ascertain the behaviour of the pyrometers at higher temperatures, no further experiments were made with zinc and tin.

Freezing Point of Magnesium.

Pyrometer.	Wt. of Mg.	t.
13 (1)	71 grams	632·8
13 (2)	69 „	632·5

The metal used was "commercial" distilled magnesium, obtained direct from the Patricroft Company. It is improbable that it contained more than 99 per cent. of the pure metal: hence, our value is, no doubt, too low.

The experiments on magnesium were discontinued for the present, owing to the rapid destruction of the pyrometer tubes and crucibles by the fused metal.

Freezing Point of Antimony.

Pyrometer.	Wt. of Sb.	
7 (1)	300 grams (commercial)	624·3
7 (2)	500	623·5
13 (1)	300	623·5
	Pure Antimony from Tartar Emetic.	
7 (3)	500 grams	629·39
16 (1)	„	629·79
7 (4)	„	629·45

The mean freezing point of antimony (pure) is 629·54°.

As we were much struck with the great discrepancy between the freezing points of our commercial antimony and the usually accepted value (440°), we made a qualitative analysis, and found that it contains considerable quantities of lead. We therefore procured some of the pure metal made from tartar emetic, and satisfied ourselves that it was free from lead, iron, and potassium. It will be seen that this pure antimony had a higher freezing point than the commercial sample, and that the discrepancy between our number and 440° was increased. It is worthy of notice that the pure antimony behaved like the pure metals, silver, gold, and copper, in having a freezing point persistent for a long time, and a melting point identical with its freezing point. The antimony was fused in a salamander cylinder placed in a small Fletcher's blast furnace, and it was protected from oxidation, when cooling, by keeping a current of coal gas passing over the surface. After fusion for six hours, the surface remained perfectly bright, like molten silver. At the end of the experiments, the freezing point was again determined with pyrometer 7 (4), and found to have undergone no change.

TABLE X.—*Freezing Point of Aluminium.*

Pyro.	Wt. of Al.	*t.*	Pyro.	Wt. of Al.	*t.*
7 (1)	68 grams	656·2	13 (3)	200 grams	654·1
(2)	282 „	654·4	(4)	180 „	655·8
8 (1)	282 „	654·6	(4)	175 „	655·0
(2)	—	655·1	(5)	175 „	655·0
(4)	175 „	654·5	(6)	175 „	654 9
13 (1)	200 „	652·5	(7)	175 „	654·1
(2)	182 „	654·0			

The mean of these values is 654·5°.

Perhaps it would be correct to reject 7 (1), on account of the small amount of metal used, and 13 (1), on account of the absence of flux, but both were good experiments, and the mean would not be altered by striking them out.

8 (3) and (5) were rejected, on account of the absence of any stir, and 8 (5) and 8 (6) on account of the kind of aluminium used in them (electrolytic from Schaffhausen), which appeared to be less pure than the metal used in the other experiments. The freezing point of aluminium is far less definite than that of the metals antimony, silver, gold, and copper. Its temperature is never quite stationary, but, during the period of solidification, falls very slowly. There is no difficulty in determining the f. p. roughly, but a sharp reading is impossible. This, no doubt, is due to the impurities present (silicon and iron) in the samples of the metal at our disposal.

The presence or absence of flux did not make a very great difference in the f. p. On some occasions we blew oxygen through the molten metal, but did not thereby alter the freezing point, although large quantities of oxide were formed. It would appear from this that the oxide is little, if at all, soluble in the metal. From the fact that the freezing point was not changed by blowing oxygen through the metal, we conclude that the impurities were not removed by the process. We found, by direct experiment, that the addition of crystalline silicon lowered the freezing point.

We generally used as a flux a fused mixture of sodium and potassium chlorides with a little cryolite. This flux underwent some chemical changes, emitting flashes of light when it was stirred, but the f. p. of the aluminium did not appear to be affected by it. The aluminium used in the experiments given in the table above was known to contain 99·5 per cent. of pure Al.

TABLE XI.—*Freezing Point of Silver.*

Pyro.	Wt. of Ag.	*t*.	Pyro.	Wt. of Ag.	*t*.
8 (1)	300 grams	958·8	13 (4)	700 (Stas)	959·4
"	"	958·8	"	"	959·5
"	"	958·8	"	"	959·4
8 (3)	298 grams	958·3	"	"	959·5
11 (1)	300 "	958·6	16 (1)	"	960·9
"	"	958·7	"	"	960·9
"	"	958·7	"	"	960·9
11 (2)	700 (Stas)	961·6	16 (2)	700 (J. & M.)	960·7
"	"	961·6	"	"	960·9
"	"	961·6	"	"	961·0
"	"	961·6	"	"	961·0
13 (2)	268 grams	957·5	16 (3)	298 (same as in 8 (3))	959·6
"	"	957·7			
"	"	957·9	"	"	959·6
13 (3)	"	958·3	16 (4)	284 (J. & M.)	960·4
"	"	958·5	"	"	960·6
"	"	958·5	"	"	960·4
"	"	958·5			

All these experiments were performed in salamander crucibles, and a little coal gas was allowed to burn in the furnace during cooling, so as to maintain a reducing atmosphere. With this precaution, there is no absorption of oxygen, and no spitting. If this precaution is neglected, as in 13 (1) and the first reading of 8 (1), the freezing point is always lower; Callendar has already observed this fact.

The 700 grams of silver used in 11 (2), 13 (4), and 16 (1) had been specially purified by us, using Stas' method of precipitation with ammoniacal cuprous sulphite. Its freezing point was exquisitely steady, and, as in the case of the gold, there was no difference between the melting and freezing points. The experiments 16 (2) and 16 (4) were performed with a new and specially pure sample of silver from Johnson and Matthey; its f. p. is the same as that of the Stas silver.

It seems probable also, from comparing 16 (4) and 16 (2), that 700 grams is better suited for an accurate determination than the smaller quantities. We therefore take, as the most probable value, the mean of 11 (2), 13 (4), 16 (1), and 16 (2), attaching equal weight to each group.

We thus get the number 960·7° for the temperature at which silver freezes.

TABLE XII.—*Freezing Point of Gold.*

Date.	Wt. of Au.	Pyro.	*d.*	*pt.*	*t*° C.
Dec. 23, 1894:					
4.20	782 grams	18	1·574	903·15	1061·5
4.45	"	"	"	902·85	1061·2
Dec. 24:					
11.40	"	13	1·500	908·60	1061·8
12.5	"	"	"	908·66	1061·9
12.25	"	"	"	908·68	1061·9
2.35	"	16*	1·532	906·74	1062·3
3.0	"	"	"	906·65	1062·2
3.16	"	"	"	906·56	1062·1
Dec. 30:					
3.53	1200 grams	15	2·04	873·1	1061·2
4.45	"	13 A	1·553	905·8	1061·9
4.50	"	"	"	"	1061·9
4.58	"	"	"	905·7	1061·8
5.5	"	"	"	"	1061·8
6.5	"	14	1·511	907·95	1062·0
6.10	"	"	"	"	1062·0
6.15	"	"	"	"	1062·0
7.15	"	18 A	1·577	902·1	1060·1

The mean freezing point of gold is 1061·7°.

In the experiments of December 23 and 24, the 782 grams of gold was contained in a small, cylindrical, clay crucible, imbedded in a larger crucible, and heated in a Fletcher blast-furnace. The immersion of the pyrometer was from 60 to 70 mm., and the rate of cooling very slow. The period of constant temperature lasted from the commencement of freezing until the gold was a solid mass, and the melting point seemed to be identical with the freezing point.

In the experiments of December 30, with 1200 grams, the gold was contained in a single wider salamander crucible, and the depth to which the pyrometer was immersed was less than 50 mm. The rate of cooling was faster, and the period of constant temperature shorter, but the f. p. could in both cases be read to $\frac{1}{100}$th of a degree. If it were not for the expense, a pot of 2000 grams of gold would afford an ideal means of obtaining the higher fixed point on platinum thermometers.

Messrs. Johnson and Matthey assayed the gold for us before the experiments; it proved to contain 99·95 per cent. of pure gold. After the experiments were finished, they again assayed the gold, and found that it had undergone no change whatever in purity.

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* A small uncertainty exists here as to the constants of 16.

TABLE XIII.—*Freezing Point of Copper.*

Pyro.	Wt. of Cu.	t° C.	Pyro.	Wt of Cu.	t° C.
7 (2)	500 grams	1079·6	8 (1)	805 grams	1079·0
"	"	1079·5	8 (2)	"	1080·6
"	"	1080·4	"	"	1080·5
"	600 grams	1081·0	11	664 grams	1081·7
"	"	1080·9	"	"	1081·5
"	"	1080·9	"	"	1081·5
"	664 grams	1081·0	"	"	1081·3
8 (1)	805 grams	1079·2	12 (1)	"	1080·3
"	"	1079·0	12 (2)	500 grams	1081·6

The mean freezing point of copper is 1080·5°.

These experiments were made in plumbago crucibles, the surface of the copper being protected from oxidation by a layer of molten borax; this layer formed a colourless glass when examined at the end of the experiment. In some cases, a little powdered charcoal was added to the borax, but this precaution does not appear to be necessary if plumbago crucibles are used. If the copper is allowed to oxidise, its f. p. is lowered, presumably by the solution of the oxide [*vide* 7 (1)].

The copper used with pyrometer 8 was the best rod and bar copper, such as is used for electrical connections. The other samples were granulated electrolytic copper from Johnson and Matthey. The pyrometer tubes were rapidly attacked by the fused borax.

Experiments on the Freezing Points of Salts.

The recent very interesting experiments of Victor Meyer, Riddle and Lamb (*Ber.*, 1894, **27**, 3129), on the melting points of salts, determined by means of an air thermometer, have led us to slightly extend our work with a view to getting another comparison with the air thermometer.

The freezing points of the salts were determined in a platinum crucible protected by an outer crucible, the space between being packed with magnesia or with broken crucible material. The porcelain tube of the pyrometer was protected from the action of the fused salts by a thin-walled platinum tube 105 mm. long, which fitted the pyrometer tube closely, like the finger of a glove.

Several sources of error were noticed.

1. The latent heat of most of the salts appears to be small, for a considerable amount of the salt crystallises before the pyrometer reaches a steady temperature.

2. Owing to the fact that the solid salt is deposited as a non-

TABLE XIV.—*Freezing Points of Salts.*

K_2SO_4

Time	Pyro.	Weight of salt.	t° C.
	13 (1)	115 grams	1061·4
	,,	,,	1058·6
3 P M	13 (2)	160 grams	1062 6
3 40	,,	,,	1062·7
4 0	,,	,,	1062 5
4 0	13 (3)	577 grams	1066·2
6 0	..	,,	1066·1
8 10	16 (1)	,,	1066·7
	,,	,,	1066 8
	,	,	1066 7
5 0	,,	,,	1066 6

Melting Point.
V. Meyer's Method.

Time	Pyro.	Weight of salt.	t° C.
12 10	16 (2)	1 gram	1083 9
12 45	,,	..	1085·5
1.3	,,	..	1084·3
1 11	,,	..	1083·2

Na_2SO_4.

Time.	Pyro.	Weight of salt.	t° C.
3 5	13 (1)	512 grams	883
3 30	,,	,,	883 3
3 55	,,	,,	883 2

Melting Point.
V. Meyer's Method.

Time.	Pyro.	Weight of salt.	t° C.
6 50	16 (1)	1 gram	902
7 5	,,	,,	901 8
7 35	,,	,,	902·0
7 50	,,	,,	901 7

Na_2CO_3.

Time	Pyro.	Weight of salt.	t° C.
4 0	13 (1)	150 grams (about)	819·4
4 45	,,	,,	818 8
5.20	,,	,,	817 9
2 32	17*	500 ,,	848·0
3 25	16 (1)	,,	845·3
6 15	16 (2)	500 grams	851 7
6 30	,,	,,	851 1
7 0	,,	,,	851 0
7 30	18 (1)	,,	849·2
7 50	,,	,,	848·4

* δ of pyrometer 17 was 2 10.

conducting layer on the surface of the pyrometer tube, which is at the same time cooling by conduction along the leads and stem, the steady temperature does not last so long as in the case of a freezing metal. For these reasons we procured a larger platinum crucible capable of holding a kilogram of the fused salts, and the only experiments we regard as trustworthy were made with large quantities in this crucible.

3. Another source of error lies in the fact that the fused salts at these high temperatures are rapidly acted on by the water vapour and reducing gases of the furnace. Our attempts to protect them were not altogether successful, owing to the necessity of keeping the crucible partly open to allow of the pyrometer being used as a stirrer, and also to the fact that platinum at high temperatures is readily permeable by gases.

The fused sulphates, when examined after the experiments, were found to be feebly alkaline, sometimes gave a black stain on a silver coin, and smelt slightly of sulphuretted hydrogen when moistened. The sodium carbonate slightly attacked the surface of the platinum, probably on account of the formation of a trace of caustic alkali.

It may be expected that changes of this kind would be roughly proportional to the duration of the experiment, and this is seen to be the case, for the f.p. of sodium carbonate becomes lower the longer it is heated. In the experiments with this salt, we can easily allow a correction for the time of heating; this gives us for the probable f.p. of freshly molten sodium carbonate a temperature very near 852°, both with pyrometers 16 and 18, and 850° for the abnormal pyrometer 17. We take 852° as the correct value, though this may turn out to be slightly too low. In the experiments with sodium carbonate, the deterioration of the salt could be watched by looking into the crucible; the first two or three times the salt was fused, it remained quite transparent, but afterwards it became opaque in consequence of some chemical change.

In the good experiments 16 (1), 13 (3), and 13 (1) with the sulphates, no progressive fall in the freezing point was detected; we therefore think that the slight chemical changes which undoubtedly occurred had no appreciable effect, and that the mean values 1066·5° for potassium sulphate and 883·2° for sodium sulphate may be accepted. The potassium sulphate used in 16 (1) was afterwards titrated with standard acid, and was found to contain 0·2 per cent. of free alkali reckoned as KOH. In a previous experiment we ascertained that 2 per cent. of sodium carbonate lowers the freezing point of potassium sulphate by 20°, and as a very rough approximation we may therefore assume that 0·2 per cent. of potassium hydroxide would cause a fall of 2°.

As the numbers we obtained for the freezing points of these salts differed from those of Meyer, Riddle, and Lamb, we determined to follow their method more closely. A sample of 1 or 2 grams of the salt was placed in a platinum test-tube 8 mm. wide and 110 mm. long, and fused at the lowest possible temperature. A platinum wire was then introduced into the fused mass, and as it solidified the wire became fixed axially in the tube. The test-tube was then secured to the pyrometer in such a position that the fused salt was on a level with and close to the coil. The pyrometer, with attached tube, was now placed in a bath, contained in our large platinum crucible, of some salt or mixture melting at a lower temperature than the salt in the tube. The free end of the platinum wire was carried over a pulley, and a weight of 50 grams attached to it. On slowly heating the furnace, the rise in temperature could be watched with the galvanometer, and at the moment when the weight pulled out the superficially-fused salt from the test-tube the temperature of the bath was taken. By repeating the experiment several times, cutting off the supply of heat while the temperature was well below that at which the pull-out took place, we could make the rise of temperature at the moment of pull-out very slow. In all cases, the wire pulled out with it the bulk or the whole of the salt.

When care is taken to make the rise in temperature of the bath very slow at the moment of pull-out, results consistent among themselves are obtained by the method, but we are disposed to think that it always gives too high a temperature. For example, with K_2SO_4 we got 1084° for the pull-out (? melting point) and 1066·5° for the freezing point, the two temperatures differing by 17·5°. Similarly, the pull-out point for sodium sulphate exceeds the freezing point by 19°. As the pull-out point is determined on a rising, and the freezing point on a falling temperature, we should expect any lag of the pyrometer to produce an opposite effect to the one observed.

We think that the freezing point method is most probably correct, and that in V. Meyer's method the temperature of the bath rises considerably above the true melting point before the wire pulls out. Notwithstanding this fact, the pull-out experiments enable us to compare our thermometry with the air thermometry of Meyer, Riddle, and Lamb (Table XV, see next page).

It will be seen that in experiments with potassium sulphate, conducted in the same way, our results agree very well with those of V. Meyer, but in the corresponding experiments with sodium sulphate we are 40° higher. It may be inferred that a pull-out experiment with sodium carbonate would have given us a reading about 20° higher than Meyer's.

It is certain that these discrepancies are not wholly due to the thermometry, but we are at present unable to localise the sources of error.

TABLE XV.

	Le Chatelier.	Victor Meyer.	Heycock and Neville.
Sodium carbonate...	810°	—	852·0°
Sodium sulphate....	867	—	883·2
Potassium sulphate..	1015	—	1066·5
	Melting Points by the Pull-out Method.		
Sodium carbonate...	—	849°	
Sodium sulphate....	-	863	902·2°
Potassium sulphate..	—	1078	1084·0

General Comparison of our Results with those obtained by other Observers.

The best recent work on the melting points of silver, gold, and copper, that we are acquainted with, is contained in a paper by Holborn and Wien, "Ueber die Messung hoher Temperaturen" (*Ann. Phys. Chem.*, 1892, 47, 107). They used a platinum rhodium couple standardised by a porcelain air thermometer.

Both their results and those of Meyer, Riddle, and Lamb, being based directly on air thermometry over the whole range studied, have a greater *à priori* claim to be regarded as standard numbers than ours, which are an extrapolation from air thermometry carried to 600° only. At the same time we would point out that a comparison of our numbers, even when obtained by pyrometers having very different constants, with those of Holborn and Wien, shows that a platinum-resistance pyrometer yields much more consistent results up to 1100° than those given by a thermo-couple.

We regard the substantial agreement of our results with those of Holborn and Wien as proving the validity of the δ formula up to 1100°. This is, perhaps, the most important result of our work.

On account of the purity of the antimony, silver, gold, and copper used by us, we attach considerable value to the freezing points found for these metals. The other metals were probably not so pure, and there may be on that account an error of a few degrees in the values given.

The following table gives a comparative view of our results, those of Holborn and Wien, and of some other recent workers. The numbers are partly taken from Holborn and Wien's paper.

COMPARATIVE TABLE XVI.

Year	1879.	1892.	1892.	1895.
Observers.	Violle.	Holborn and Wien.	Callendar and Griffiths.	Heycock and Neville.
Tin	—	—	231·7	231·9
Zinc	—	—	417·6	418·96*
Antimony ..	—	—	—	629·54
Magnesium..	—	—	—	632·6
Aluminium .	625	—	—	654·5
Silver.......	954	968	972·0†	960·7
Gold	1035	1072	—	1061·7
Copper	1054	1082	—	1080·5

SECTION IV.

Determination of the Ice Point R_0.—For this purpose, we use a double copper cylinder, the inner cylinder being 250 mm. high and 100 mm. in diameter, with the interval between the two cylinders packed with felt.

The ice is crushed to a fine powder by hammering it between folds of dry sail-cloth; it is then washed, drained, and transferred to the inner copper cylinder. Water from *previously melted ice* is now poured on it, and the ice and water well stirred together. The excess of water is drained off by a tube attached to the lower end of the cylinder until the water level is about an inch below the top of the ice.

Great care must be taken to remove all soluble salts from the surface of the pyrometer tube before introducing it into the ice. The measurement of the resistance can be made when the pyrometer has been in the ice about five minutes.

Determination of the Steam Point R_{100}.—We use a hypsometer of the ordinary form, except that it is provided at the side with a wide reflux condenser, so arranged as to deliver the condensed water into the boiler below the surface of the boiling water. Some arrangement of this sort is necessary, otherwise the steam would condense on the head of the pyrometer and injure the insulation.

Since a change of 27 mm. in the barometer produces a change of 1° in the boiling point of water in the neighbourhood of 100°, we see that $\frac{dt}{dp} = 0{\cdot}037^\circ$ per millimetre. If the thermometer is one whose fundamental interval is within 1° of 100, we can at once reduce

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* Meyer and Riddle by the air thermometer get 419° for the melting point of zinc (*Ber.*, 1893, 26, 2443).

† This number is not given by Callendar, but it can be deduced from the data he gives (*Phil. Mag.*, Feb., 1892).

R_{100} to what it would have been at a pressure of 760 mm. (see Table IV).

It is absolutely necessary that the surface of the pyrometer should be free from all soluble salts when the steam point is being taken.

We used a special form of compensated sulphuric acid barometer, made by Hicks, of Hatton Garden. This barometer is the invention of Professor Callendar, and is described by him in the *Phil. Mag.*, January, 1894. It has a very open scale, one division being equal to 0·188 mm. of mercury, and is therefore much more suitable for our work than an ordinary mercury barometer. Mr. Griffiths kindly compared it daily for some weeks with his standard mercury barometer. A scale of comparison was then plotted in such a way that the readings were at once obtained on the mercury scale reduced to 0° and sea level in latitude 45.

Determination of the Sulphur Point R_s.—Besides finding the constants R_0 and R_{100} for a platinum pyrometer, it is necessary, in order to obtain the constant δ in the equation

$$t - pt = \delta\{(t/100)^2 - t/100\},$$

to find the resistance at some other known temperature, which should be at a considerable distance above R_{100}. We have followed Callendar and Griffiths in choosing the boiling point of sulphur, and in the details of the method pursued.

In order to obtain with accuracy a fixed point on a thermometer immersed in boiling sulphur vapour, it is necessary to pay attention to numerous small details. The following method gives the most satisfactory results.

The vessel containing the sulphur, Fig. 3, resembles the outer boiling tube of a Victor Meyer's vapour density apparatus. It is 48 cm. long by 5 cm. diameter, with a bulb at the bottom 6—7 cm. in diameter, and is made of hard glass.

The tube passes through the axis of a cone of asbestos card, the space between the cone and the tube being packed with asbestos wool. This outer cone, which is 36 cm. long and 15 cm. wide at the base, serves as a jacket, to prevent either too rapid cooling of the sulphur vapour or its superheating by the flame of the lamp. It is necessary that the liquid sulphur should reach 4 or 5 cm. up the boiling tube, in order that any superheated sulphur vapour may be washed by the liquid sulphur out of contact with the overheated walls of the bulb. If this precaution be neglected, consistent results cannot be obtained. With a single large-sized Bunsen, and using 260 grams of sulphur, it takes about 1½ hours before the sulphur vapour appears above the top edge of the outer asbestos cone.

The pyrometer is placed in the axis of the glass tube, as shown in the figure, and it is absolutely necessary to protect the part containing the platinum spiral by means of a cone of thin asbestos, constructed as follows. Asbestos card, about $\frac{1}{16}$ in. thick, is rolled into a cone 10 cm. long, with its base just wide enough to fit loosely the inside of the glass tube. This cone is stitched together with iron wire, and is perforated near its apex with three or four holes about $\frac{1}{2}$ in. in diameter. The base of the cone is closed with a plate of asbestos, perforated at its edges, as shown in the plan B of Fig. 3.* By means of this inner cone, which is bound to the pyrometer with iron wire, the sulphur vapour is made to take the path indicated by the arrows, whilst the liquid sulphur condensed above trickles either down the walls of the glass tube or over the surface of the cone, *without flowing over the bulb.*

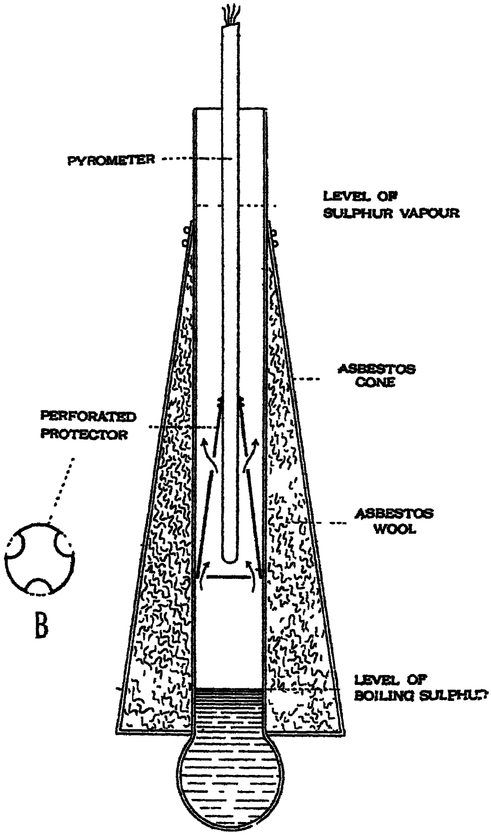

FIG. 3.—Section of sulphur-boiling apparatus showing pyrometer and inner cone.

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* This inner cone is referred to in the tables as the "perforated protector."

A pyrometer immersed in the sulphur vapour acquires the temperature in about 10 minutes, and will not show a change of more than 0·02° in the course of several hours, provided the barometer is steady. If the sulphur is allowed to solidify in the bulb, it can be remelted by withdrawing the glass tube from the outer cone and heating it round the surface of the sulphur, and not at the bottom of the bulb. If this simple precaution be adopted, the same tube will serve for some dozens of determinations. When the pyrometer is in the sulphur vapour, the mouth of the tube is closed with asbestos card. The sulphur used in our experiments was kindly given to us by Mr. Allhusen, of Newcastle, and was chemically pure; it was obtained by the partial combustion of sulphuretted hydrogen.

Since the *pt* temperature of boiling sulphur varies with the height of the barometer, it is necessary to introduce a correction. From Regnault's experiments we get the change of temperature due to a small change of pressure in the neighbourhood of the boiling point.

$$\frac{dt}{dp} = 0{\cdot}082^\circ \text{ C. per mm.}$$

This holds approximately for a change of 10 mm., either above or below the boiling point. An example will show most clearly how this pressure correction is applied.

Example.—Pyrometer 16 on December 21 had the following constants.

R_0 .... 288·347. R_{100} .... 391·734. R_s .... 723·788.

Bar. .. 762·04. Since $\frac{dt}{dp} = 0{\cdot}082$ per mm., the sulphur was boiling at a temperature of

$$444{\cdot}53 + 0{\cdot}082 \times 2{\cdot}04 = 444{\cdot}7.$$

Again, since $pt = \frac{Rt - R_0}{R_{100} - R_0} \times 100$, we get

$$Pt_s = \frac{(723{\cdot}788 - 288{\cdot}347) \times 100}{391{\cdot}734 - 288{\cdot}347}$$

$$= \frac{435{\cdot}441 \times 100}{103{\cdot}387}$$

$$= 421{\cdot}176.$$

Hence, substituting in the formula

$$t - pt = \delta\, t/100(t/100 - 1), \text{ we get}$$

$$444{\cdot}7 - 421{\cdot}176 = \delta\, 4{\cdot}447 \times 3{\cdot}447, \text{ therefore,}$$

$$\delta = \frac{23{\cdot}524}{15{\cdot}328} = 1{\cdot}5347$$

We wish here to express our indebtedness to the Grant Committee of the Royal Society for their liberality in placing at our disposal a sum of money for the purchase of instruments.

To Messrs. Johnson and Matthey for lending us, free of all charge, the considerable quantity of gold necessary for our experiments, for making the assays, and for valuable information concerning the metals we have used.

To Mr. Horace Darwin, of the Cambridge Scientific Instrument Company, for the care and accuracy with which he has constructed the thermometers and other apparatus.

To Mr. E. H. Griffiths for much valuable advice concerning the thermometers, and also for practical assistance in some of the later experiments.

[*Note as to the purity of the copper used in the experiments with Pyrometers* 7, 11, *and* 12.—Messrs. Johnson and Matthey have made a special assay of the electrolytic copper mentioned on p. 190, and find that it contains 99·95 per cent. of copper. We have estimated the iron in 10 grams, and found 0·04 per cent.]

Sidney Sussex College,
Cambridge.

XXII.—*Action of Potassium Cyanide Solutions on New Zealand Gold and Silver.*

By J. S.* Maclaurin, B.Sc., University College, Auckland, New Zealand.

The present contribution is a continuation of a paper printed in the Transactions for 1893 (**63**, 724), in which the action between gold and potassium cyanide, the basis of the now extensively applied Macarthur-Forrest or Cassel process, was investigated, and in which it was proved, 1st, that oxygen is necessary for the dissolution of gold in potassium cyanide solutions, and that it combines with the potassium of the potassium cyanide in the proportions required by the equation $4Au + 8KCN + 2OH_2 + O_2 = 4AuCN,KCN + 4KOH$. 2nd. That the rate of dissolution of gold in potassium cyanide solutions varies with the concentration; increasing as the solution becomes more dilute until it reaches a maximum at about 5 per cent., below which the rate of dissolution of the gold falls off, and that this remarkable variation may be explained by the fact that the solubility of oxygen in such solutions decreases as the concentration increases, whereby the solvent power of the strong solutions is rendered less than that of the weaker solutions which are capable of taking up more oxygen.

As these results appeared to warrant further investigation, I continued my experiments, as detailed in the following pages.

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* In the last contribution, these initials were erroneously printed R. C.

In the paper already referred to, an experiment to prove the necessity of oxygen for the dissolution of gold in potassium cyanide is described. and it is shown that when precautions were taken to exclude oxygen, a gold plate lost only 0 0002 gram in 24 hours, whilst, when the same solution was exposed to the air, the plate lost 0·00835 gram in the same time. In order to get more convincing proof on this point, I prepared gold paper by steeping filter paper in a solution of gold trichloride, containing $\frac{1}{10}$th per cent of gold, suspending the moist paper horizontally over ammonia, and reducing the oxide thus formed by immersion in a hot solution of oxalic acid (Skey, *Trans. N.Z. Inst.*, 25, 383). After washing and drying, the paper had a uniform pink tint. A piece, $\frac{1}{2}$ in. square, containing about 0·00002 gram of gold, was introduced into the limb of a Dumas bulb which had been two-thirds filled with a 5 per cent. solution of potassium cyanide. The end of the limb was then drawn out to a small diameter, and the cyanide solution boiled briskly during an hour, after which the boiling was considerably slackened and the point of the limb sealed with the blowpipe; when the solution had cooled, the gold paper was shaken into it. In the first experiment, the colour in the paper faded before the limb was sealed. I concluded that this was due to the combined action of oxygen and hydrocyanic acid, the latter being evolved in small quantity by the boiling solution, and condensing in the cold part of the limb where the gold paper was placed. In a second experiment, I therefore kept the limb hot enough to prevent condensation of the hydrocyanic acid; this proved entirely successful, as, after the limb had been sealed, the gold paper, when shaken into the cooled solution, appeared to have lost none of its colour. Next day, however, the colour had faded a little, but it required eight days to make the gold paper as colourless as a piece of plain filter paper which had been introduced along with it for comparison. Or, in other words, it required eight days to dissolve 0·00002 gram of gold. The point of the limb was now broken, the solution well shaken to saturate it with air, and a piece of gold paper, in every respect similar to that used in the first part of the experiment, introduced into the bulb. The colour of this paper faded completely in two minutes. This experiment can leave no doubt as to the absolute necessity of oxygen in order to bring about dissolution of gold.

As the results given in Tables V and VI (Trans., 1893, 63, 731) are insufficient to completely determine the law governing the dissolution of gold in solutions of cyanides of varying strengths, I made the following additional series of experiments.

In the former experiments, a single gold plate was used for each determination, and the results show a certain amount of irregularity.

Four plates were now taken and dealt with as follows. The plates numbered 1 and 2 were suspended by cotton in a small flask containing a 50 per cent. cyanide solution, those numbered 3 and 4 in a similar flask containing a 40 per cent. solution. Purified air was aspirated through the two flasks. The losses sustained by the plates are given in the following table.

TABLE I.

	50 per cent. KCN.		40 per cent. KCN.	
Numbers on plates	1	2	3	4
Loss of gold in two hours.	0·00195	0 00125	0·00405	0·00485

When the plates 1 and 2 were placed in the 40 per cent. solution, and 3 and 4 in the 50 per cent. solution, the results were as follows.

TABLE II.

	50 per cent. KCN.		40 per cent. KCN.	
Numbers on plates	3	4	1	2
Loss of gold in two hours.	0·00135	0·00245	0·0035	0·0025

From these numbers, it appears that there is considerable variation in the amount of gold dissolved from apparently similar plates. In order to get more concordant results, I remelted several of the plates, and dividing the button into four parts, rolled and stamped these into plates as already described. With these plates, and using two large Woulff's bottles in place of the small flasks employed in the last experiments, a considerable number of determinations were made; 100 c.c. of cyanide solution was put into each of these bottles and kept at a constant temperature by immersion in a small tank of water. The results, although agreeing much more closely than those just given, still varied considerably. I therefore modified the experiment by bending the points of the inlet tubes at right angles, so as to keep the solutions more thoroughly agitated than before. Eight determinations were made, using this method, but with no better results.

As it seemed probable that the irregularity of the results was due to small bubbles of air being carried in varying numbers to the different plates, it was necessary to devise some process by which the cyanide solution could be thoroughly agitated and kept saturated with air without the possibility of air bubbles in suspension coming in contact with the gold plates. The apparatus shown in Fig. 1 meets these requirements. A regular stream of air driven by a filter pump through several solutions of potassium hydrate up a tower containing coke saturated with that solution, and then through three flasks containing barium hydrate solution, issues from the drawn-out point of the tube C, and passing into the open end of the tube D, carries a stream of cyanide solution into the bottle B, where it is syphoned back by E, and thus a constant circulation of the solution is maintained The vessels A and B stood in a small tank containing water at 18°. From preliminary experiments, it had been found that when there is little cyanide solution the oxygen is withdrawn from the solution by the gold more rapidly than it is absorbed, even when the stream of air is rapid. In the present series of experiments, I therefore used a large amount of solution (500 c c), and reduced the duration of the experiment to one hour.

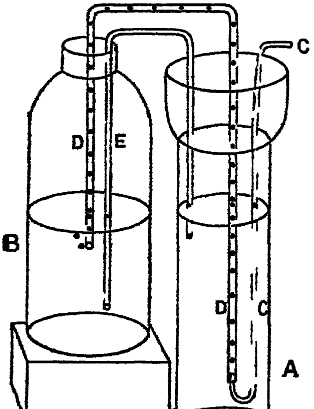


FIG. 1.

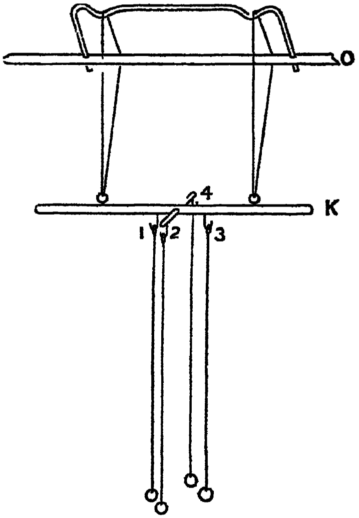


FIG 2.

The cyanide solution was saturated at 18° with air by shaking vigorously for five minutes in a 40-ounce stoppered bottle, removing the stopper several times to equalise the pressure. The bottle fitted into a small wool-lined box, and, with due precautions, it was an easy matter to have the temperature of the contained solution, 18°, at the close of the shaking. The gold plates were suspended by cotton from the hooks attached to the beam K, Fig. 2, which was itself suspended from the crank H fixed to the shaft O of a small water wheel driven at 20 revolutions per minute by a carefully regulated supply of water. These plates were dropped into the solution in A, and the cotton suspenders being always made the same length, the plates were at the same depth in all the experiments, being about an inch from the bottom in their lowest position, and two inches in their highest. The preliminary experiments with this apparatus showed slight differences in the losses of the four plates in the same solution. Thus, in two hours, with 50 per cent. solution, the losses were 0·001025, 0·00115, 0·001075, 0·00095; with 45 per cent., 0·001175, 0·001575, 0·001625, 0·00125; and with 35 per cent., 0·00225, 0·0023, 0·002275, 0·002175.

In these experiments, No. 1 plate hung from No. 1 hook, No. 2 plate from No. 2 hook, and so on. Thinking there might be differences in the rate of motion of the solution in proximity to the respective plates, owing to the syphon coming in at one side of the vessel A, the positions of the plates were altered, putting No. 1 plate on No. 2 hook, and so on, these different arrangements being repeated many times, but it was not observed that a plate in one position sustained a greater loss than in any other. After exposure to the cyanide solution, the plates were rapidly washed under the tap, and then with distilled water, roughly dried with filter paper, and heated to low redness by holding them with iron forceps in a Bunsen flame. As the different degrees of heating and different rates of cooling to which the four plates were subjected might affect their rates of dissolution in cyanide, 12 experiments were made in which everything was conducted as before, except that the plates, after being washed with water and then with alcohol, were dried at a low temperature. The results were no more concordant than before.

In order to discover if these slight irregularities in the results were due to impurities in the plates, I prepared some gold by the method adopted by Professor Thorpe when determining the atomic weight of that metal. Two plates were made from this purified gold, in the manner already described, but these, when exposed to the action of cyanide solution under varying conditions, differed slightly in their losses just as the old plates had done. These plates, with two of the old ones, were subjected to the action of cyanide solutions in eight experiments, and sustained the following total losses. New plates, 0·0402, 0·0415 gram; old plates, 0·0392, 0·0409 gram.

Finally I abandoned the attempt to get absolute agreement among the plates, and resolved to make up for the want of this by multiplying the number of determinations and taking the mean of the results. The numbers so found are shown in Table III, and graphically on pp. 205 and 206, Plates I and II.

These results show that the rate of dissolution of gold in solutions

TABLE III.

KCN. Grams per 100 c.c.	Gold dissolved.	KCN. Grams per 100 c.c.	Gold dissolved.	KCN. Grams per 100 c.c.	Gold dissolved	KCN. Grams per 100 c.c.	Gold dissolved.
50	0·00050	20	0·00277	4	0·00600	0·1	0·00675
45	0·00064	15	0·00350	3	0·00613	0·05	0·00666
40	0·00091	10	0·00440	2	0·00627	0·02	0·00613
35	0·00124	8	0·00488	1	0·00650	0·01	0·00345
30	0·00163	6	0·00537	0·5	0·00670	0·005	0·00030
25	0·00210	5	0·00572	0·25	0·00654		

of potassium cyanide gradually increases as the concentration of the solution decreases, reaches a maximum at 0·25 per cent. solution, and again decreases.

As it seemed desirable to determine whether another metal would show similar variations in its rate of dissolution in cyanide, the following experiments were made with silver plates. These were of the same size as the gold plates, and were prepared from the chloride. On exposing them to the action of cyanide solution, the losses of the four plates varied slightly; as in the case of the gold. Their positions were changed, some determinations were made without blowing air through the solution; washing with alcohol and drying at a low temperature, instead of heating to redness, was also tried; and, lastly, the four plates were connected by a silver wire, but through all these varying methods there were slight differences in the losses of the plates. Sometimes one plate would lose more than any of the others in each of several determinations, and then another would head the list for a few experiments, only to give place to a third; at other times, the plates varied in their losses from experiment to experiment.

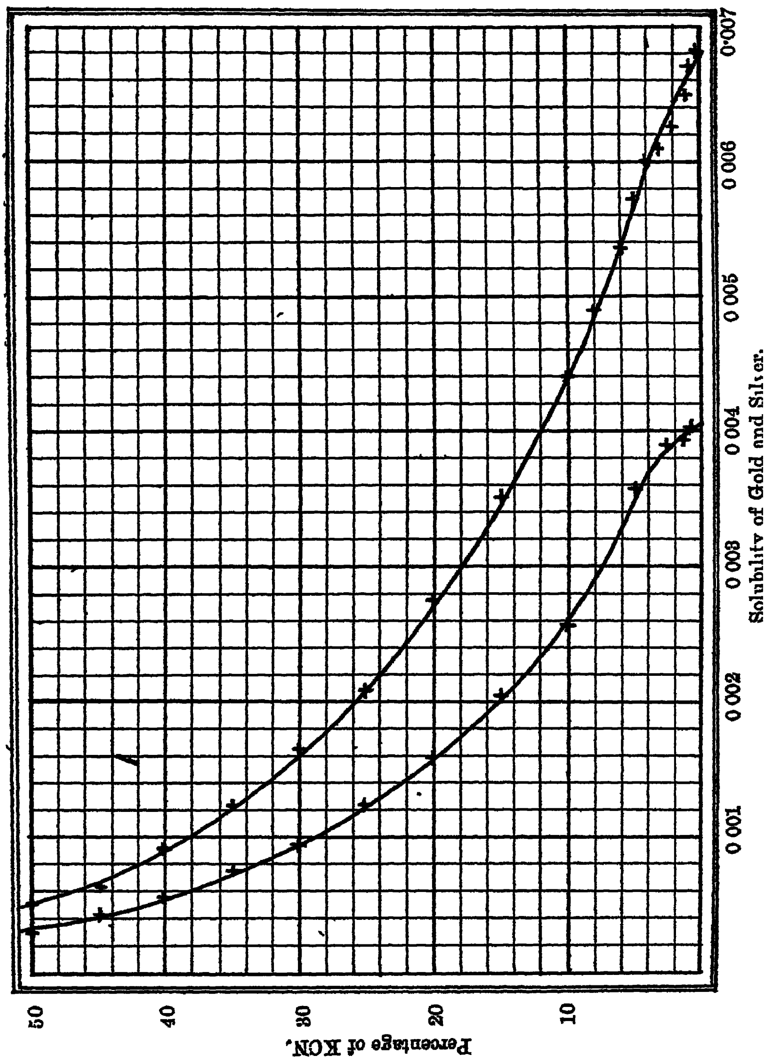
As in the case of gold, I finally gave up the attempt to get absolute

TABLE IV.

KCN. Grams per 100 c.c.	Silver dissolved.	KCN. Grams per 100 c.c.	Silver dissolved.	KCN. Grams per 100 c.c.	Silver dissolved.	KCN. Grams per 100 c.c.	Silver dissolved.
50	0·00033	25	0·00125	2·5	0·00393	0·05	0·00380
45	0·00044	20	0·00159	1	0·00395	0·02	0·00285
40	0·00056	15	0·00205	0·5	0·00400	0·01	0·00213
35	0·00073	10	0·00257	0·25	0·00410	0·005	0·00040
30	0·00097	5	0·00356	0·10	0·00396		

agreement among the plates, and was forced to make a large number of determinations, and to take the mean of these in compiling Table

PLATE I



IV, and in drawing the curve shown in Plates I and II. The results so obtained are comparable with those shown for gold, since, in both cases, the plates were the same size and the conditions of experiment exactly the same.

The results given in this table show that the rate of dissolution of silver in solutions of potassium cyanide gradually increases as the concentration of the solution decreases, reaches a maximum at 0·25 per cent. solution, and again decreases. These changes in the rate of dissolution are similar to those shown by the gold plates, and the point of maximum solubility is the same. Further, the ratio

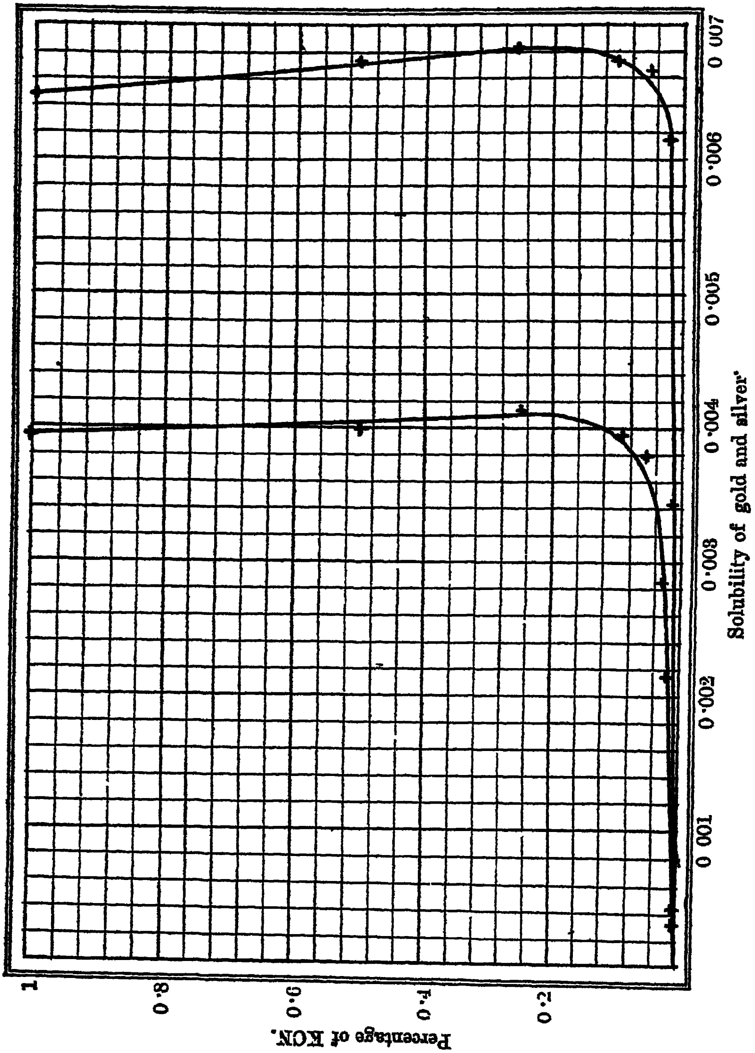


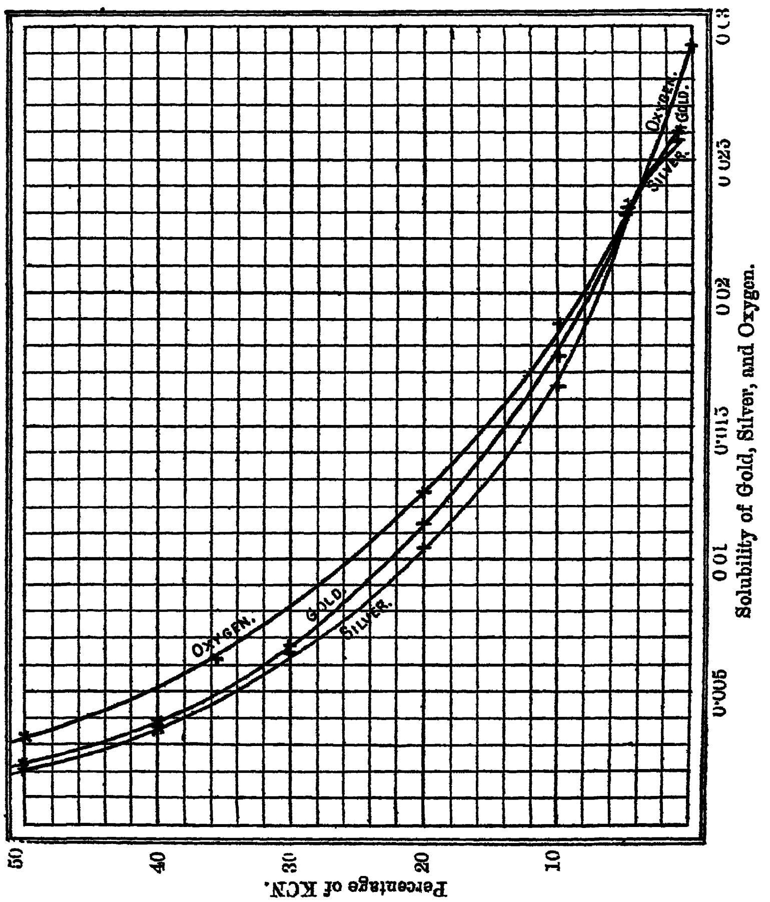
PLATE II.

of the gold to the silver, dissolved by any particular strength of cyanide solution, is approximately that of their atomic weights.

These remarkable variations in the solubility of gold and silver may be explained as already stated (p. 199), by the fact that the solubility of oxygen in cyanide solutions decreases as the concentration increases, and that thus the solvent power of the strong solutions is rendered less than that of the weaker solutions, which are capable of taking up more oxygen.

In Plate III, I have redrawn the curve, showing the absorption coefficients of oxygen in cyanide solutions, and have placed beside it

Plate III



the curves representing the solubility of gold and silver. In order to make these comparable, the scale on which gold is represented in

Plates I and II has been increased four times, and that for silver six and a half times.

In Table VI (p. 211), the relations of the gold and silver to the oxygen are shown under the headings Au/O and Ag/O (found). On considering these, it is evident that the solubilities of the two metals are dependent on that of oxygen. Now, if the amount of gold or silver dissolved depends solely on the amount of oxygen in solution, the values Au/O and Ag/O should be constant; but in the results found it will be seen that these values differ considerably, gradually decreasing as the concentration increases. Therefore, in the more concentrated solutions there is less metal dissolved than the amount of oxygen in solution appears to demand. This points to some retarding action on the motion of the oxygen molecules. Now, it seemed probable that viscosity has such a retarding action on the motion of the oxygen molecules in solution, reducing their velocity, and consequently diminishing the number of impacts on the surfaces of the plates in a given time, and so decreasing the amount of gold or silver dissolved. In order to test the validity of this conclusion, the rates of dissolution of gold and silver were determined in cyanide solutions rendered more viscous by the addition of various substances such as sugar and glycerol, which might be assumed to exert no chemical influence on the solubility of these metals. The results are shown in Table V. As it was found that the coefficients of absorption of oxygen for solutions containing equivalent proportions of sugar and of potassium cyanide are approximately the same only a few of the coefficients shown in this table were determined, the majority being calculated from the curve showing the solubility of oxygen in potassium cyanide solutions.

TABLE V.

	Grams per 100 c c.	KCN. Grams per 100 c c.	Dissolved in one hour.		Oxygen coefficients of absorption.	Au/O.
			Gold.	Silver.		
Sugar	0	1	0·00650	0·00395	0·028	0·232
„	5·26	1	0·00488	—	0·025	0·195
„	15·78	1	0·00333	—	0·022	0·151
„	26·30	1	0·00243	—	0·021	0·116
„	36·82	1	0·00152	—	0·019	0·080
„	26·30	5	0·00211	—	0·0187	0·113
Glycerol	14·15	10	0·00223	—	0·0171	0·130
Gum acacia .	1·0	1	0·00492	0·00342		
Gelatin	1·0	1	0·00374	0·00250		
Starch	1·0	1	0·00443	0·00270		

The results in this table, and especially those in the column Au/O, prove very conclusively that the assumption as to the retarding action of viscosity was correct.

Suppose now that we consider the number of times in a second a given oxygen molecule strikes a surface. We may assume from the results just given that this will depend on the viscosity coefficient z, or, in other words, will be a function of z. So that if N be the number, we can write $N = a + bz + cz^2 + \&c.$, where a, b, and c are independent of z (Maclaurin's theorem); or since Au/O, Ag/O are dependent on the number of impacts in unit of time, we can write $Au/O = a + bz + cz^2 + \&c.$, and $Ag/O = a_1 + b_1z + c_1z^2 + \&c.$

In order to ascertain if these relations hold good for the values of Au, Ag, and O, found, I determined the coefficients of viscosity of a number of cyanide solutions. The observations were made by Gartenmeister's method (*Zeit. physik. Chem.*, 6, 524), using Finkener's formula $z = \frac{r^4\pi p}{8lv} - \frac{vs}{8\pi gl}$. In this expression, r is the radius and l the length of a capillary tube through which a volume v of the liquid of sp. gr. s flows, under a pressure p in unit of time. In my apparatus, Fig. 3, the constants were as follows. $r = 0{\cdot}23477$ mm.; $p = (h + h_1)s = (HC + CB)s = (318{\cdot}4\text{ mm.} + 31{\cdot}34\text{ mm.})s = 349{\cdot}74\,s$; $l = \pi H = 300$ mm.; $v = V/t$ (where V is volume of bulb in c.c. and t is time of flow in seconds) $= 6{\cdot}88832/t$. The value of h_1 was found by measuring with a cathetometer the height BC when half the weight of water contained between A and C had flown out. The trustworthiness of the apparatus employed was tested by determining the value for water, which was found to be 0·108842 at 18°, a value which corresponds well with Gartenmeister's number when corrected for temperature.

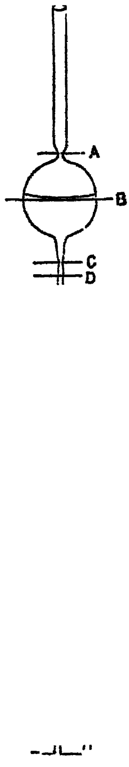


FIG. 3

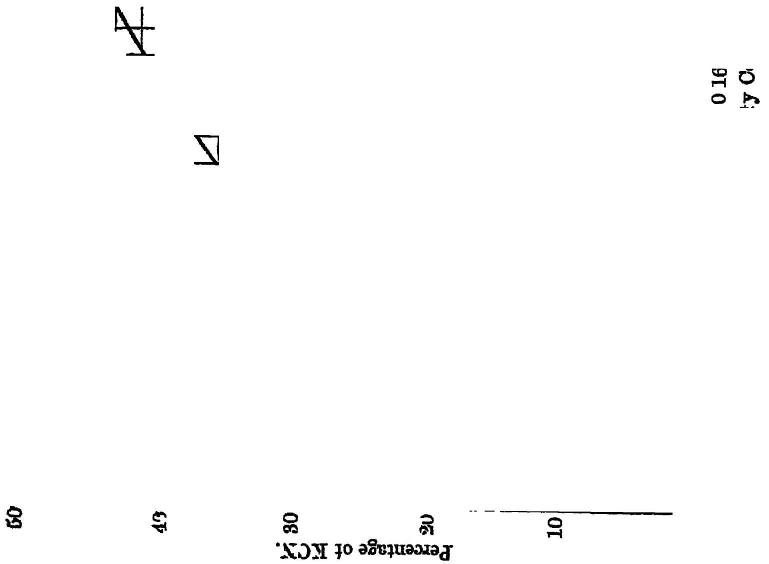
[*Note.*—There is an error in Gartenmeister's calculation of the value of the second part of Finkener's formula. In his paper, he gives for his first pipette the following constants.

$V = 8{\cdot}1015$ c.c.; $r = 0{\cdot}31842$ mm.; $l = 335{\cdot}2$ mm.; $h = 354{\cdot}4$ mm.; and $h_1 = 17{\cdot}4$ mm.; and calculates for z the value $0{\cdot}0_3 55267\, s.t. - \frac{0\ 09803\, s}{t}$, whereas it should be $0{\cdot}0_3 552715\, s.t. - \frac{0{\cdot}0_1 9803\, s}{t}$.

This error makes his values slightly smaller than they should be; thus, for water at 20° he finds $z =$

0 1030, whereas from his determinations and a correct use of the formula he should have obtained $z = 0{\cdot}1035$.]

The values at 18° of z—the coefficient of viscosity—for 5, 10, 20, 30, 40, and 49 per cent. solutions are represented graphically in Plate IV, and, by the aid of the curve so obtained, the intermediate values were calculated, and placed together with those found by direct experiment under z in Table VI. In the same manner, the undetermined values for oxygen have been calculated from the curve representing the solubility of oxygen, and the results, together with the original determinations, are embodied in this table.



Under Au/O and Ag/O are shown the values found, and also those calculated by the aid of Maclaurin's theorem; that is to say, by the

TABLE VI.

KCN. Grams per 100 c.c.	Dissolved in one hour.		Oxygen coefficients of absorption.	Found.		Calculated.		z.
	Gold.	Silver.		Au/O.	Ag/O.	Au/O.	Ag/O.	
50	0·00050	0·00033	0·0032	0·156	0·103	0·154	0·102	0·1962
45	0·00064	0·00044	0·0040	0·160	0·110	0·172	0·110	0·1760
40	0·00091	0·00056	0·0049	0·185	0·114	0·188	0·117	0·1581
35	0·00124	0·00073	0·00625	0·198	0·117	0·201	0·123	0·1439
30	0·00163	0·00097	0·0079	0·206	0·123	0·210	0·127	0·1336
25	0·00210	0·00125	0·0100	0·210	0·125	0·217	0·130	0·1252
20	0·00277	0·00159	0·0124	0·223	0·128	0·223	0·133	0·1188
15	0·00350	0·00205	0·0152	0·230	0·135	0·227	0·134	0·1144
10	0·00410	0·00257	0·0185	0·238	0·139	0·230	0·136	0·1107
5	0·00572	0·00356	0·0230	0·248	0·154	0·232	0·136	0·1091
1	0·00650	0·00395	0·0280	0·232	0·141	0·232	0·136	0·1089

formula $\mathrm{Au/O} = a + bz + \&c.$, where $a = 0{\cdot}33$ and $b = -0{\cdot}9$, and $\mathrm{Ag/O} = a_1 + b_1 z + \&c.$, where $a_1 = 0{\cdot}18$ and $b_1 = -0{\cdot}4$.

The close agreement of the values found by these two methods is sufficient to prove that the true explanation of the smaller solubility of the gold and silver relatively to the oxygen in the more concentrated solutions is to be found in the greater viscosity of these solutions.

The following is a summary of the results obtained in this and the former paper.

1. Oxygen is necessary for the dissolution of gold in potassium cyanide, and no gold is dissolved in its absence.

2. The ratio of the gold dissolved to the oxygen required for its dissolution is 196 : 8 as demanded by the equation $4\mathrm{Au} + 8\mathrm{KCN} + \mathrm{O_2} + 2\mathrm{OH_2} = 4\mathrm{AuCN,KCN} + 4\mathrm{KOH}$.

3. The rate of dissolution of gold in potassium cyanide solutions varies with the strength of the solution, being small for concentrated solutions, increasing as the solution becomes more dilute, reaching a maximum at 0·25 per cent. of cyanide, and then again diminishing.

4. The rate of dissolution of silver in potassium cyanide varies in the same way, and the maximum is reached at the same degree of dilution.

5. The ratio of the amount of gold dissolved by any given cyanide solution to that of the silver dissolved by the same solution is nearly the ratio of their atomic weights.

6. The variation in the rate of dissolution of gold in cyanide solutions is not directly influenced by the amount of cyanide in solution, except in the case of very dilute solutions, but is mainly

due to the solubility of oxygen in these solutions, the amount of gold dissolved being nearly proportional to the absorption coefficients of oxygen in such solutions.

7 The rate of dissolution of gold is, however, not exactly proportional to the above-mentioned coefficients, but is rather less than it should be for the more concentrated solutions.

8. The explanation of this diminishing ratio of the gold dissolved to the oxygen available, as the concentration of the solution increases, is to be found in the increasing viscosity of the solutions as the quantity of cyanide augments.

9. The explanations given in 6, 7, and 8 are equally applicable to the dissolution of silver in potassium cyanide solutions.

TABLE VI.

KCN. Grams per 100 c.c.	Dissolved in one hour.		Oxygen coefficients of absorption.	Found.		Calculated.		z.
	Gold.	Silver.		Au/O.	Ag/O.	Au/O.	Ag O.	
50	0·00050	0·00033	0·0032	0·156	0·103	0·154	0·102	0·1962
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40	0·00091	0·00056	0·0049	0·185	0·114	0·188	0·117	0·1581
35	0·00124	0·00073	0·00625	0·198	0·117	0·201	0·123	0·1439
30	0·00163	0·00097	0·0079	0·206	0·123	0·210	0·127	0·1336
25	0·00210	0·00125	0·0100	0·210	0·125	0·217	0·130	0·1252
20	0·00277	0·00159	0·0124	0·223	0·128	0·223	0·133	0·1188
15	0·00350	0·00205	0·0152	0·230	0·135	0·227	0·134	0·1141
10	0·00410	0·00257	0·0185	0·238	0·139	0·230	0·136	0·1107
5	0·00572	0·00356	0·0230	0·248	0·154	0·232	0·136	0·1091
1	0·00650	0·00395	0·0280	0·232	0·141	0·232	0·136	0·1089

formula Au/O = $a + bz$ + &c., where $a = 0·33$ and $b = -0·9$, and Ag/O = $a_1 + b_1z$ + &c., where $a_1 = 0·18$ and $b_1 = -0·4$.

The close agreement of the values found by these two methods is sufficient to prove that the true explanation of the smaller solubility of the gold and silver relatively to the oxygen in the more concentrated solutions is to be found in the greater viscosity of these solutions.

The following is a summary of the results obtained in this and the former paper.

1. Oxygen is necessary for the dissolution of gold in potassium cyanide, and no gold is dissolved in its absence.

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3. The rate of dissolution of gold in potassium cyanide solutions varies with the strength of the solution, being small for concentrated solutions, increasing as the solution becomes more dilute, reaching a maximum at 0·25 per cent. of cyanide, and then again diminishing.

4. The rate of dissolution of silver in potassium cyanide varies in the same way, and the maximum is reached at the same degree of dilution.

5. The ratio of the amount of gold dissolved by any given cyanide solution to that of the silver dissolved by the same solution is nearly the ratio of their atomic weights.

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due to the solubility of oxygen in these solutions, the amount of gold dissolved being nearly proportional to the absorption coefficients of oxygen in such solutions.

7. The rate of dissolution of gold is, however, not exactly proportional to the above-mentioned coefficients, but is rather less than it should be for the more concentrated solutions.

8. The explanation of this diminishing ratio of the gold dissolved to the oxygen available, as the concentration of the solution increases, is to be found in the increasing viscosity of the solutions as the quantity of cyanide augments.

9. The explanations given in 6, 7, and 8 are equally applicable to the dissolution of silver in potassium cyanide solutions.

XXIII.—*Octacetylmaltose.*

By Arthur R. Ling and Julian L. Baker.

In the course of an investigation of the "Acetyl Derivatives of the Sugars" now being made by one of us, an octacetyl derivative of maltose has been obtained which differs in some of its properties from that described by Herzfeld. As, however, our methods of preparation were not quite identical, we subsequently followed this chemist's instructions as far as we could ascertain them, the result being that the same compound was obtained in both cases. Having acetylated maltose under a variety of conditions, and having obtained one and the same octacetyl derivative in all cases, we are forced to conclude that Herzfeld's description of octacetylmaltose is not strictly accurate.

We will now briefly refer to Herzfeld's papers on the derivative in question. He first prepared it in 1880 (*Ber.*, **13**, 267), and later (*Annalen*, 1883, **220**, 215) published a more minute description of its properties. It was obtained by boiling dry maltose with anhydrous sodium acetate (1 part) and acetic anhydride (3 parts) in a reflux apparatus for three-quarters of an hour. The author states that it crystallises from alcohol in colourless prisms, melts and decomposes at 150—155°, has a bitter taste, and is readily soluble in ether, hot alcohol, glacial acetic acid, and benzene, sparingly in carbon bisulphide, but insoluble in cold water and chloroform.

Preparation of Octacetylmaltose.—Pure maltose (10 grams) is well mixed in a mortar with anhydrous sodium acetate (10 grams), and the pulverised mixture introduced into a flask; acetic anhydride (20 c.c.) is then poured on to the mixture, and the whole heated to incipient boiling. A very violent action occurs, which continues for about a minute, when it will be found that the whole of the solid substance has dissolved. The solution, after being boiled for about 5 minutes to complete the acetylation, is poured into a large volume of water, and the syrupy precipitate which separates is repeatedly washed by decantation with small quantities of water; this causes it to become more viscid, and finally it solidifies. It is then drained as completely as possible from the water, dissolved in 90 per cent. alcohol, and the solution repeatedly evaporated with fresh quantities of alcohol until it is quite free from acetic acid. The product is dissolved in 90 per cent. alcohol, and placed in a desiccator over concentrated sulphuric acid, when crystals begin to be formed at the end of 12 hours or less; these are prismatic needles, and in some cases stout prisms.

Mr. W. J. Pope kindly examined some of the latter for us crystallographically, with the following results.

The crystals consist of fragments of orthorhombic prisms, and are several mm. in length and about 0·5 mm. in thickness: the end faces of the crystals are absent, having apparently been broken off. The forms present are $m\{110\}$, $m_1\{890\}$, and $m_{11}\{1\,30\,0\}$, and the prisms appear as if striated perpendicular to the *c*-axis; this appearance would seem to be due to cracks rather than to ordinary striations. The forms $m\{110\}$ and $m_1\{890\}$ are much more largely developed than the prism $m_{11}\{1\,30\,0\}$.

On examining the crystals in the polarising microscope, the extinction is found to be parallel to the *c*-axis; under a $\frac{1}{12}$th oil immersion objective, the biaxial interference figure is seen emerging through one of the faces of the form $m_{11}\{1\,30\,0\}$. The optic axial plane is therefore parallel to the pinacoid $a\{100\}$. The axial angle is small, and the double refraction positive and weak. The dispersion is slight, and the angle for red light greater than that for blue.

Crystalline System: Orthorhombic.

$a : b : c = 0{\cdot}8670 : 1 : ?$

Forms present—

m .. .. $\{110\}$,
m_1 .... $\{890\}$,
m_{11}.......... $\{1\,30\,0\}$.

	Angles.	No. of observations.	Limits.	Mean.	Calc.
mm =	$110 : 1\bar{1}0$	10	81° 28′—82° 11′	81° 51′	—
mm_1 =	$110 : 890$	14	3 6— 3 57	3 36	3° 22′
m_1m_{11} =	$890 : 1\,30\,0$	9	43 6—43 51	43 28	43 31
$m_{11}m_{11}$ =	$1\,30\,0 : \bar{1}\,30\,0$	11	4 6— 4 41	4 23	4 24

The observations recorded here differ altogether from those of Herzfeld (*loc. cit.*), as if this preparation of octacetylmaltose were not chemically identical with the one here described.

The crystals of octacetylmaltose are collected after a lapse of 24 hours, and recrystallised from alcohol, the solution being treated, if necessary, with animal charcoal free from ash constituents. Prepared in this way, it forms magnificent, long, prismatic needles, and melts at 158—159° without undergoing decomposition. It is insoluble in cold water, and only very slightly soluble in boiling water; it is sparingly soluble in carbon bisulphide and cold alcohol as stated by Herzfeld, but dissolves readily in the boiling solvent; contrary to Herzfeld's observation, however, we find that it is extremely soluble in chloroform; it also dissolves in ether, glacial acetic acid, and benzene. The compound is devoid of taste. The analytical values obtained with several specimens are as follows.

0·1031 gave 0·1853 CO_2 and 0·0537 H_2O. C = 49·01; H = 5·78.
0·1084 „ 0·1942 CO_2 and 0·0576 H_2O. C = 48·85; H = 5·90.
0·1047 „ 0·1885 CO_2 and 0·0555 H_2O. C = 49·09; H = 5·86.

0·5270 gram was heated for 4½ hours in a Lintner's pressure flask with 20 c.c. of normal hydrochloric acid, and, after cooling, exactly 20 c.c. of normal sodium hydroxide solution was run in, and the acetic acid titrated with a standard solution of barium hydroxide [1 c.c. = 0·008078 acetic acid], of which it required 46 c.c. This corresponds with 71·15 per cent. of acetic acid.

0·5154, as in the last experiment, required 44·9 c.c. of standard barium hydroxide solution; acetic acid = 70·56 per cent.

$C_{12}H_{14}(OAc)_8O_3$ requires C = 49·55; H = 5·60; acetic acid = 70·79 per cent.

A determination of the molecular weight by the cryoscopic method gave the following result.

0·5726 gram dissolved in 15·078 grams of benzene gave a depression of 0·300°. M.W. = 632·8. $C_{12}H_{14}(OAc)_8O_3$ requires 678 per cent.

Specific Rotatory Power. No birotation was observed.

I. 1·2625 grams dissolved in chloroform, and the solution made up with that solvent to 25 c.c. at 15·5°, read 6·3° in a 200mm. tube, employing a Laurent polarimeter and sodium light. $[\alpha]_D$ = +62·37.

II. 0·9017 gram dissolved in chloroform, and made up to 25 c.c. at 15·5, read 2·4° in a 100mm. tube. $[\alpha]_D$ = +62·07.

A specimen of octacetylmaltose, prepared by Herzfeld's method, was found to be identical in all respects with the substance just described; it melted at 158—159°, and had a specific rotatory power in chloroform solution of $[\alpha]_D$ = +62·05.

Herzfeld (*Annalen*, 220, 218) states that the specific rotatory power of octacetylmaltose (0·5 gram dissolved in 25 c.c. of alcohol) is $[\alpha]_D$ +81·8. It was found impossible to prepare so concentrated an alcoholic solution of our compound as the one just quoted. We have, however, obtained the following values for the specific rotatory power in alcoholic solution.

0·4269 gram dissolved in 93 per cent. alcohol, and the solution made up with the same solvent to 50 c.c. at 15·5°, read 1·01° in a 200 mm. tube, whence $[\alpha]_D = +59·14$. A second determination in alcoholic solution gave $[\alpha]_D = +50·39$.

In order to see whether more than eight acetyl groups can be introduced into the maltose molecule, 0·5 gram of octacetylmaltose was mixed with an equal weight of anhydrous sodium acetate, and the mixture boiled with 15 c.c. of acetic anhydride for 1½ hours in a reflux apparatus. The product, when crystallised from alcohol, melted at 157—158°, and was found to be unaltered in every respect.

We have made numerous experiments to ascertain if an isomeric octacetylmaltose is formed when maltose is boiled with zinc chloride and acetic anhydride. The product consists of a small quantity of crystalline octacetylmaltose (m. p. 158—159°), together with an amorphous substance, which has resisted all attempts to obtain it in a crystalline condition; it appears to have the composition of an octacetylmaltose.

A description of so well-defined a compound as octacetylmaltose cannot, we think, fail to be of interest to chemists.

Chemical Laboratory,
London Beetroot Sugar Association.

XXIV.—*Action of Heat on Ethylic β-Amidocrotonate.*
Part II.

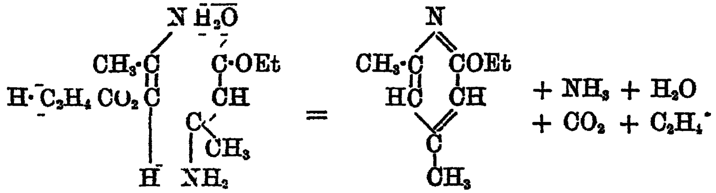
By J. Norman Collie, Ph.D., F.R.S.E.

In two different papers (*Annalen*, 1884, **226**, 297, and Trans., 1891. **59**, 172), I have drawn attention to the easy manner in which ethylic β-amidocrotonate may be made to yield condensation compounds. Since then, from time to time, I have returned to work at this substance, sometimes to prepare pyridine derivatives which I had need of in other researches, sometimes in order to see whether any light might be thrown on the constitution of pyridine itself.

In Part I of this paper, it was shown that during the purification of ethylic β-amidocrotonate by distillation under reduced pressure, a crystalline compound of the formula $C_{10}H_{13}NO_3$ was always produced in small quantities. This substance I pointed out was probably ethylic lutidonecarboxylate,* and was formed by a reaction precisely similar to that which gives rise to dehydracetic acid when ethylic acetoacetate is distilled.

I was unfortunately only able to obtain this ethereal salt in small quantities as a bye-product, and the results which are now brought forward are the outcome of various attempts to produce this compound in larger quantities. The primary object has not been successful, for I have been unable to improve on the process; other compounds, however, have been formed by the action of heat on the amidocrotonate, which are not without interest, for they show how condensation may occur in many ways, and produce substances belonging to widely different types.

The chief product of the destructive distillation of ethylic β-amidocrotonate seems to be ethoxylutidine,



But besides this compound a dimethylpyrrol is also formed apparently identical with the dimethylpyrrol obtained by the distillation of gelatin.

A third substance also has been isolated, which is doubtless a pyridine derivative, but, unfortunately, it could only be obtained in very small quantity, and partly for this reason and partly because it seemed to belong to a new class of compounds I have been unable to satisfactorily discover its exact constitution. It is formed from 2 mols. of ethylic β-amidocrotonate by condensation,

$$2C_6H_{11}NO_2 = CH_3\cdot COOEt + EtOH + C_6H_8N_2O.$$

When heated with zinc dust, it gives α-picoline and ammonia; it is a monacid base, and, when treated with phosphorus pentachloride, it yields a monochloride. Judging from this behaviour, it is probably a hydroxyamidopicoline having one or other of the following formulæ.

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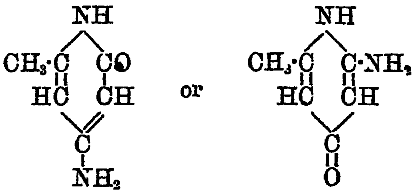
* I may mention that when a solution of an acid, $C_8H_8O_4$ (which was first prepared by Frist by acting on the dichloride of dehydracetic acid with sulphuric acid), is allowed to evaporate with strong aqueous ammonia, the ammonium salt of the lutidonecarboxylic acid is produced.



It is not diazotised when treated with fuming hydrochloric or sulphuric acid, and sodium nitrite, but it may be noted that α- and γ-amidopyridine also are extremely difficult to diazotise. It yields a curious compound when treated with the oxides of nitrogen prepared from nitric acid and arsenious oxide.

$$C_6H_8N_2O + H_2O + NO_2 = C_6H_{10}N_3O_4.$$

The action of heat, therefore, on ethylic β-amidocrotonate gives rise to four different nitrogenous condensation products.

1. Ethylic lutidonemonocarboxylate, $C_{10}H_{13}NO_3$.
2. Dimethylpyrrol, C_6H_9N.
3. Ethoxylutidine, $C_9H_{13}NO$.
4. Hydroxyamidopicoline (?), $C_6H_8N_2O$.

EXPERIMENTAL PART.

When ethylic β-amidocrotonate is heated under a pressure of 90—100 mm. it distils between 153—155° with very slight decomposition (*loc. cit.*). If, however, it is rapidly heated at ordinary atmospheric pressure, a very small portion may be distilled at a temperature above 200°, but the greater portion is decomposed.

Several trials were made in order to find out the best method for obtaining some clue to the manner in which the ethylic β-amidocrotonate was decomposed by the agency of heat. Bearing in mind the fact that dehydracetic acid can be prepared from ethylic acetoacetate when its vapour is passed through a heated tube, the vapour of the amidocrotonate was subjected to the same treatment, first at the ordinary pressure and then under a pressure of about 100 mm. of mercury. This treatment, however, proved to be much too violent, for much charring took place in the tube whilst large quantities of gas were also evolved. Next a flask, containing 200 grams of the amidocrotonate, was connected with a condenser and heated in an oil bath, a thermometer being placed in the fused amidocrotonate to mark at what temperature the decomposition began. At 160°, distillation commenced, and ammonium carbamate was formed which sublimed in white needle-shaped crystals inside the condenser. The temperature was kept below 200° for about three hours, during which time 100 grams of liquid (A) distilled. The flask was then taken out of the oil bath, and its contents rapidly distilled; between 200° and 360° much gas was evolved (carbon dioxide and ethylene), and a further quantity (B) of distillate was collected, weighing 65 grams, whilst there remained in the flask 35 grams of a black charred mass.

Portion A proved to be almost entirely alcohol, ethylic acetate and acetone, for when shaken with excess of water it all dissolved, and on saturating with salt most of the ethylic acetate separated. After drying and fractionating, the latter boiled at 76—78°, possessed the characteristic odour, and gave the ordinary reactions for ethylic acetate. The residual aqueous solution was then distilled; the first portion of the distillate gave the acetone, which, after purification, was recognised by its boiling point and crystalline compound with sodium hydrogen sulphite, whilst the second fraction, boiling between 75° and 80°, proved to be nearly pure alcohol. Methylamine was very carefully searched for, but without success, all the nitrogen present in portion A being present in the form of ammonium carbamate.

As no pyridine derivative or other condensation products had been found in portion A, the distillate which had come over between 200° and 360° was next investigated. This fraction, B, was a brown and viscous substance interspersed with some crystalline matter. It partly dissolved in water, and the solution when warmed with soda gave only traces of ammonia, but on testing it for nitrogen that element was found to be present in considerable quantity. The aqueous solution was treated with caustic soda, warmed, filtered, and acidified with sulphuric acid, but no insoluble acid was obtained, which would have been the case if any lutidonecarboxylic acid had been present. When the resin was allowed to stand in contact with air, the brown colour gradually changed to a brilliant grass-green.

Various attempts were made to extract pure substances from this somewhat uninviting material, but without much success. When subjected to fractional distillation, it began to boil at about 200°, and between that temperature and 240° a considerable amount passed over into the condenser, whilst the portion which distilled between 280—320° was semi-crystalline, and the residue in the flask began to char rapidly. Another experiment was therefore tried to see whether better results could be obtained by gradually heating the amidocrotonate in an oil bath to 180°, and then examining the residue in the flask for condensation products. As in the previous experiment, about half the contents of the flask passed over slowly, the distillate being alcohol, acetone, and ethylic acetate; the dark-brown residue was viscous, and would not crystallise, neither could any crystalline compound be obtained from it by treatment with various solvents. When it was warmed with caustic soda solution, some ammonia was evolved, together with alcohol. As the latter seemed to point to the presence of an ethereal salt, the solution was rendered slightly acid with sulphuric acid and the precipitated resin removed by treatment with ether. The aqueous solution on being concentrated soon deposited a little crystalline matter, which was recrystallised from alcohol and water. The crystals were small and granular, acid to litmus, and melted at 254—256° (corr.), with evolution of carbon dioxide, showing that the substance was evidently lutidonemonocarboxylic acid (Trans., 1891, **59**, 176); 0·6 gram of the acid, when fused, yielded 75 c.c. of carbon dioxide, the theoretical amount for the following equation.

$$C_5HN(OH)(CH_3)_2{\cdot}COOH = C_5H_2N(OH)(CH_3)_2 + CO_2,$$

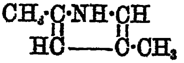
being a little over 80 c c. The residue of αα′-dimethylpyridone in the flask was then distilled; it boiled above 300°, and its melting point was found to be 231—232° (corr.), this proving beyond doubt that the resin contained small quantities of lutidonemonocarboxylic acid.

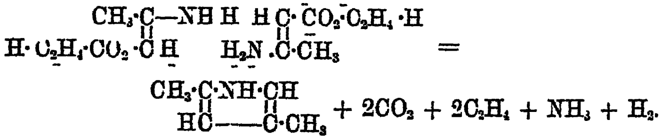
Ultimately, after many trials, it was found that the only way the resin could be made to yield any considerable amount of condensation products which were pure enough to analyse, was by distillation. To give one out of the many experiments made, 50 grams of the brown resin was distilled as rapidly as possible until only a black charred tar remained behind in the flask. During the distillation, carbon dioxide and ethylene gases were given off in large quantities. The yellow distillate, which became semi-solid, was then extracted with cold acetone, as the solvent left most of the crystalline matter undissolved; as, however, this crystalline compound was formed in small quantity, it was only by collecting the product of many experiments that enough was obtained for purification. The substance, when pure, melted at 194° (corr.); it will be described later in the paper.

The portion soluble in acetone was first investigated. After the acetone had been evaporated, an oily residue was left (20 grams) which contained basic nitrogen compounds. It was therefore made alkaline with strong solution of soda, and steam was blown through the liquid so long as anything volatile passed over with it. The residue in the flask was then rendered just acid with sulphuric acid, and after the black tar which was precipitated had been filtered off the aqueous solution was concentrated; it deposited a small quantity of lutidonemonocarboxylic acid. The steam distillate separated into two layers, an oil and water; it was shaken with ether, and the ethereal solution dried quickly with a little solid soda and distilled. After the ether had distilled, the temperature rose rapidly to 180°, and above 230 only a very small quantity remained in the flask. As the distillate gave the pyrrol reaction with pine wood saturated with hydrochloric acid, it was quickly shaken with hydrochloric acid, when a small quantity only of a pyrrol-derivative remained undissolved, nearly the whole of the oil combining with the acid to form a soluble salt. After several experiments, enough of the pyrrol was obtained to distil. It boiled between 170° and 175°, and oxidised in the air, turning yellow; when warmed with ferric chloride, it gave a reddish coloration.

0·250 gave 0·696 CO_2 and 0·214 H_2O. C = 75·9; H = 9·5.
C_6H_9N requires C = 75·8; H = 9·5 per cent.

The substance is, therefore, a dimethylpyrrol, and seems to be identical with the dimethylpyrrol obtained by Knorr (*Annalen*, 1887, **236**, 326) from isonitrosoethylic β-amidocrotonate. Knorr's compound possesses the following properties: b. p. 171°; with ferric chloride, it gives a cherry-red colour on warming, and it possesses a blue fluorescence. I did not notice, however, any fluorescence in the pyrrol I had obtained, but perhaps this may be due to the fact that the compound never was obtained quite colourless. Probably identical with this dimethylpyrrol is the one obtained by Ciamician and Wiedel (*Ber.*, 1879, **13**, 299) from the products of dry distillation of gelatin.

Knorr assigns the formula  $\begin{array}{l}CH_3{\cdot}C{\cdot}NH{\cdot}CH\\ \quad HC{=\!=\!=}C{\cdot}CH_3\end{array}$ to it, and its formation from ethylic β-amidocrotonate is easy of explanation.



$$\begin{array}{l}\qquad\quad CH_3{\cdot}C{-}NH\;H\quad H\,C{\cdot}CO_2{\cdot}C_2H_4{\cdot}H\\ H{\cdot}C_2H_4{\cdot}CO_2{\cdot}C\,H\qquad H_2N{\cdot}C{\cdot}CH_3\qquad =\\ \qquad\qquad CH_3{\cdot}C{\cdot}NH{\cdot}CH\\ \qquad\qquad\quad HC{=\!=\!=}C{\cdot}CH_3 + 2CO_2 + 2C_2H_4 + NH_3 + H_2.\end{array}$$

Probably the hydrogen is not evolved as such during the distillation of the amidocrotonate, but is oxidised to water or reduces some other product of the action.

When the hydrochloric acid solution, from which the dimethylpyrrol had been separated, was treated with soda, it yielded a considerable quantity (15 grams) of an oil insoluble in water; when this was fractionated, about half of it passed over between 215° and 220° (corr.). An analysis of this fraction was therefore made.

0·309 gave 29 c.c. moist nitrogen at 16° and 777 mm. N = 11·1.
0·216 „ 0·5565 CO_2 and 0·173 H_2O. C = 70·6; H = 8·8.

From the appearance of the substance, it seemed probable that it was an ethoxylutidine, but the above results do not quite agree with those required by a compound of the formula $C_5NH_2(CH_3)_2·OEt$, namely, C = 71·5; H = 8·6; N = 9·2. As it yielded a platinochloride which crystallised well, this salt was used to purify it. After several recrystallisations, the platinum salt seemed to be pure, melting constantly at 226—228° (corr.) with much blackening. An analysis gave the following numbers.

0·276 gave 0·075 Pt. Pt = 27·1. 0·248 gave 0·068 Pt. Pt = 27·3.
0·410 „ 0·458 CO_2 and 0·1555 H_2O. C = 30·4; H = 4·2.
0·383 „ 0·1045 Pt and 0·385 AgCl. Pt = 27·2; Cl = 29·8.
0·3435 „ 11·8 c.c. moist nitrogen at 16° and 757 mm. N = 3·9.

	C.	H.	N.	Cl.	Pt.
Calculated for $(C_9H_{13}NO)_2,H_2PtCl_6$	30·3	3·9	3·9	29·9	27·4
Found........................	30·4	4·2	3·9	29·8	27·2

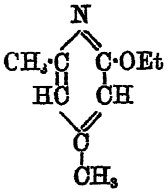
Another analysis of the undried salt was made. It was found to lose 2·0 per cent. of water of crystallisation when heated at 130°, and to contain 26·6 per cent. Pt. If the salt crystallised with 1 mol. of water, $(C_9H_{13}NO)_2,H_2PtCl_6,H_2O$, it would require Pt = 26·9, H_2O = 2·4. The formula is that of the platinochloride from ethoxylutidine, $C_5NH_2(CH_3)_2·OEt$.

In order to prepare the ethoxylutidine from the impure material, the pure platinum salt was first obtained from it, and then decomposed by means of sulphuretted hydrogen. The solution containing the hydrochloride of the base was filtered from the sulphide of platinum and evaporated. Caustic soda liberated free ethoxylutidine, which was distilled with steam, collected, dried over soda, and found to boil between 217° and 218° (corr.). A combustion was made.

0·2745 gave 0·719 CO_2 and 0·221 H_2O. C = 71·4. H = 8·6.
$C_5NH_2(CH_3)_2·OEt$ requires C = 71·5; H = 8·6 per cent.

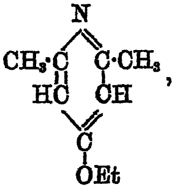
It only remained, therefore, to determine which ethoxylutidine it was. As it was produced from ethylic β-amidocrotonate, there are only two alternatives. It must be either

I.



or

II.



and had been produced according to the equation $2C_8H_{11}NO_2$ $C_9H_{13}NO + C_2H_5·OH + NH_3 + CO_2$.

That it has the formula I is proved by the following facts. When heated with hydriodic acid in a sealed tube at 140°, the ethyl group is replaced by hydrogen, and Hantzsch's pseudolutidostyril (*Ber.*, **17**, 2904), together with ethylic iodide, is obtained. The pseudolutidostyril was converted into the platinum salt, which was dried and analysed.

0·2545 gave 0·0745 Pt. Pt = 29·6.
$(C_7H_9NO)_2,H_2PtCl_6$ requires Pt = 29·6 per cent.

Also some pure pseudolutidostyril, prepared by another method (*Ber.*, 1887, **20**, 447), was treated with phosphorus pentachloride in order to prepare the corresponding chlorolutidine. This chlorolutidine gave with sodium ethylate a substance identical with the ethoxylutidine obtained by the action of heat on ethylic β-amidocrotonate.

The only product, therefore, remaining to be investigated was the compound melting at 194°, which separated in crystals from the distillate of the amidocrotonate. It is not formed in nearly such large quantities as the ethoxylutidine, and it was only after several distillations that enough was obtained for investigation. It was purified by dissolving it in hot alcohol and precipitating with acetone; it then formed white crystals melting at 194—195° (corr.). When carefully heated, it can be partially sublimed.

0·3310 gave 0·701 CO_2 and 0·1930 H_2O. C = 57·8; H = 6·4.
0·4175 ,, 0·895 ,, 0·2615 ,, C = 58·4; H = 6·9.
0·3050 ,, 58 c.c. moist nitrogen at 15° and 752 mm. N = 22·1.
0·1275 ,, 23·5 ,, ,, at 14° and 765 ,, N = 21·8.
0·1500 ,, 30 ,, ,, at 19° and 761 ,, N = 22·9.

	Calculated for $C_6H_8N_2O$.	Found.				
		I.	II.	III.	IV.	V.
C	58·1	57·8	58·4	—	—	—
H.........	6·4	6·4	6·9	—	—	—
N	22·6	—	—	22·1	21·8	22·9

The platinum salt crystallised in short, thick needles.

0·2460 lost at 130° 0·0120 H_2O. H_2O = 4·8.
1·6990 ,, ,, 0·0875 ,, H_2O = 5·1.
0·2460 gave 0·0695 Pt. Pt = 28·3.
0·2885 ,, 0·0805 ,, Pt = 27·9.
$(C_6H_8N_2O)_2,H_2PtCl_6 2H_2O$ requires Pt = 27·9; $2H_2O$ = 5·1 per cent.

An analysis of the dry salt was also made; it contained 29·7 per cent. Pt. Theory requires 29·5.

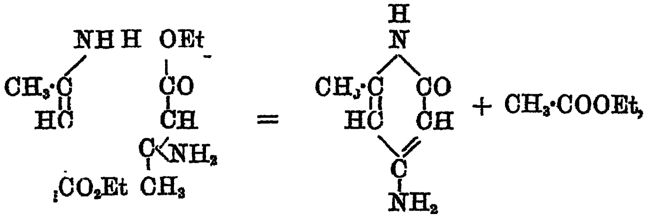
The hydrochloride was next prepared. Excess of hydrochloric acid was added to the substance, and the solution evaporated to dryness over a water bath; the mass of small needle-shaped crystals which remained had no melting point, but sublimed when heated, leaving no residue.

0·22 took 13·8 c.c. N/10 $AgNO_3$ solution. Cl = 22·2

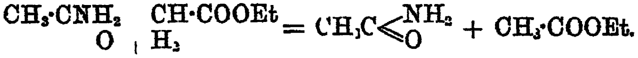
$C_6H_8N_2O,HCl$ requires Cl = 22·1 per cent.

When the hydrochloride is heated with a little zinc dust, a very pungent smell is produced, resembling that of mice or acetamide mixed with pyridine. The original substance (m. p. 194°) does not yield a trace of ammonia even when boiled with the strongest solution of soda, but when fused with solid soda, ammonia is produced. When warmed with a little sodium, the substance is only partially attacked, some of it subliming on to the upper part of the tube; a strong smell of pyridine is at the same time produced, mixed, however, with the same mouse-like smell which was noticed when the hydrochloride was heated with zinc dust.

From the above properties the substance is probably a pyridine derivative, and as it contains two atoms of nitrogen it may be a hydroxyamidopyridine. There are two reactions which might yield such a compound, firstly,

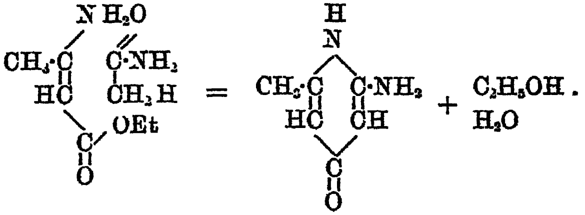


and, secondly, possibly water formed by the decomposition acts on the amidocrotonate, splitting it up into ethylic acetate and acetamide.



$$\begin{matrix}CH_3\cdot CNH_2 & CH\cdot COOEt\\ O & H_2\end{matrix} = CH_3C{<}^{NH_2}_{O} + CH_3\cdot COOEt.$$

The acetamide at the moment of its formation reacts with the amidocrotonate.



The latter alternative seems the more probable. In either case, the result is a hydroxyamidopicoline, and also, in both formulæ, if the NH_2 group were replaced by OH the dihydroxypicoline would be obtained, which substance I have already prepared from the lactone of triacetic acid and ammonia (Trans., 1892, 61, 721). Unfortunately I have not been able to effect this change, as the hydroxyamidopicoline seems to be a very stable substance. At present very little is known about the amido-derivatives of pyridine. Marckwald (*Ber.*, 1894, **27**, 1317) has prepared the α- and γ-compounds of pyridine; he finds that they do not diazotise in aqueous solutions. They have an alkaline reaction. He has also made γ-amidolutidine. The only way in which he has been able to displace the NH_2 group by OH, is by dissolving the substance in strong sulphuric acid or fuming hydrochloric acid, and adding concentrated sodium nitrite solution drop by drop. Tin and hydrochloric acid do not affect them. The only other reference to amidopyridines is by H. Meyer (*Kais. Acad. d. Wissenschaft in Wien*, Bd. 103, Abth. II b., März, 1894); he applies the Hofmann reaction to the amide of picolinic acid, and from it obtains amidopyridine. I have made many attempts to diazotise the substance (m. p. 194°); the first was with oxides of nitrogen prepared by the action of nitric acid on arsenious acid. The compound was dissolved in water, and excess of oxides of nitrogen added; the solution, after evaporation, left a well-crystallised substance, which did not resemble either the original compound or dihydroxypicoline. It dissolves easily in water, has a strongly acid reaction, and melts at 173° (corr.) with evolution of carbon dioxide and nitric oxide.

0·288 took 15·8 c.c. N/10 soda solution. M.W. = 182 of the substance is monobasic.

0·2625 gram lowered the melting point of 24·62 grams acetic acid 0·22°. From which the molecular weight is 189.

0·186 gave 0·2595 CO_2 and 0·895 H_2O. C = 38·1; H = 5·3.

0·205 „ 40·6 c.c. moist nitrogen at 17° and 744 mm. N = 22·5.

$C_6H_{10}N_3O_4$ requires C = 38·3; H = 5·3; N = 22·3 per cent.

Possibly, therefore, this substance has been formed by the joint action of nitrogen peroxide and water.

$$C_6H_8N_2O + NO_2 + H_2O = C_6H_{10}N_3O_4.$$

By reduction with tin and hydrochloric acid, a considerable quantity of ammonia was formed, for after freeing the solution from tin by sulphuretted hydrogen, evaporating nearly to dryness, and making alkaline with soda, ammonia was at once observed. After the ammonia had been removed, the residue was made acid again with hydrochloric acid, and platinum chloride added; the resulting platinochloride, after purification, was found to contain 5·2 per cent. H_2O and 27·7 per cent. Pt, and was, in fact, the platinochloride of the original compound (m. p. 194°). This nitro-compound does not contain free nitric acid, and is not formed when nitric acid is added to the original substance (m. p. 194°).

Further attempts to diazotise the original compound by dissolving it in fuming hydrochloric acid or sulphuric acid and adding a strong solution of sodium nitrite were either without effect, or the compound was completely destroyed. The original compound is not changed when heated in a sealed tube with fuming hydrochloric acid. The compound was next treated with phosphorus pentachloride; 1 gram was dissolved in a few drops of phosphorus oxychloride, 1 gram of phosphorus pentachloride added, and the whole heated for a short time on a water bath. By this means a residue was left which, when treated with sodium carbonate and distilled, gave a distillate possessing a most powerful smell resembling mice and acetamide. As the aqueous distillate contained no insoluble oil, it was shaken up with ether, and the ethereal solution, after drying, yielded a few drops of a liquid boiling between 175° and 178° (corr.); this liquid fumed with hydrochloric acid, and gave a hydrochloride very soluble in water. The aqueous solution only gave a crystalline platinochloride when very concentrated. After recrystallisation the salt was analysed. It was first dried at 110°, when it lost 4·9 per cent. H_2O; two molecules of water of crystallisation require $H_2O = 4·9$. The dried salt gave the following results.

0·173 gave 0·0485 Pt. Pt = 28·0.
0·232 „ 0·170 CO_2 and 0·042 H_2O. C = 19·9; H = 2·0.
$(C_6H_7N_2Cl)_2,H_2PtCl_6$ requires C = 20·8; H = 2·1; Pt = 28·1,

As a last experiment, the action of zinc dust at a red heat was tried. Two grams was mixed with 10 grams of zinc dust; this mixture was placed at the back of a tube containing a column of zinc dust, and the whole heated to redness whilst a current of hydrogen was passed slowly through the tube; in this way a pyridine base was obtained mixed with ammonia. The ammonia was removed from the distillate by boiling it with nitrohydrochloric acid, and the free base was afterwards liberated with soda and distilled. It was soluble in cold water and possessed the characteristic odour of picoline. Its platinochloride melted at 210—212°, and on analysis gave 32·1 per cent. Pt; the melting point of α-picoline platinochloride is given by Ladenburg as 178°, but I have shown elsewhere (Trans., 1892, 61, 727) that this is too low, the true melting point being probably 221—222°. As I had no more of the substance I was forced to conclude my experiments with it.

The compound melting at 194° is not produced when acetamide and ethylic amidocrotonate are heated together, neither could I obtain it by heating dihydroxypicoline with the strongest ammonia solution.

Whether it is an amidohydroxypicoline or not, I am unable to say at present, but from the above-mentioned properties it seems very probable that such is the case.

University College,
London.

XXV.—*The Acid Sulphate of Hydroxylamine.*

By Edward Divers, M.D., F.R.S., Imperial University, Japan.

It is somewhat remarkable that although several hydrochlorides of hydroxylamine have been described by Lossen, the acid sulphate seems never to have been prepared.

It is well known that if more sulphuric acid is present in an aqueous solution of hydroxylamine than is sufficient to form the normal salt, the addition of alcohol will cause this, and not the acid salt to crystallise out, just as when added to acid ammonium sulphate it precipitates the normal sulphate. Unless alcohol is added, a very acid solution of hydroxylamine sulphate often refuses to deposit anything; by attention, however, to a few details it can be made to yield crystals of the acid sulphate.

Solid hydroxylamine hydrochloride is treated with, as near as may be, the quantity of sulphuric acid calculated to form the acid salt, $(NH_3O)H_2SO_4$; the mixing is effected in a dish sufficiently large to avoid loss by frothing, and the mixture is heated for some hours on the water bath until all hydrochloric acid has been expelled. The resulting clear solution becomes viscid when cold, and refuses to yield the normal sulphate, and when a particle of this salt is dropt on to its surface it is slowly dissolved. If, however, it is left to stand uncovered in a dry, cold atmosphere,[*] and the vessel occasionally moved about, crystallisation suddenly sets in, and the solution becomes traversed by long prisms which almost fill it. Left in a desiccator for a couple of days more, it becomes a translucent cake of damp crystals. The crystals are very deliquescent, and, after crushing and pressure between porous tiles, yield results on analysis which prove them to be the acid sulphate of hydroxylamine.

The analysis of the salt was effected by titrating it with sodium hydroxide, using methyl-orange as indicator, since the normal sulphate is neutral to it. The sulphuric acid was weighed as barium sulphate.

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[*] Such as that of many winter days in Tokyo, Japan, when calcium chloride in an open vessel hardly deliquesces in a week, and caustic potash can be weighed in an uncovered scale-pan. In England, the atmosphere will be too damp, and a desiccated atmosphere will be necessary.

	Calculated.	Found.
Hydroxylamine......	25·19	24·02
Sulphuric acid......	74·81	72 68
	100·00	96·70

XXVI.—*Mercury and Bismuth Hypophosphites.*

By Seihachi Hada, Graduate of the Imperial University, Tokyo, Japan.

It is probable that Rose's well-known observation in 1827 that mercuric chloride is reduced by a solution of hypophosphorous acid, first to mercurous chloride and then to metallic mercury, is the cause of no attempts having been made to prepare a mercury hypophosphite, as there seemed to be but little chance of success. At the suggestion of Dr. Divers, to whom I am much indebted for advice, I have tried the effect of using the nitrates of mercury, and in the course of my experiments have obtained the salt which is described below.

Mercurous Nitrate Hypophosphite.

This double salt is the only mercury-derivative of hypophosphorous acid I have been able to prepare; it is precipitated on adding a solution of potassium or barium hypophosphite to a solution of mercuric or mercurous nitrate. but the mercury solution must not be too dilute, and as free from acid as possible; care must also be taken to avoid using excess of the hypophosphite. The compound is not obtained when the mercury nitrate solution is added to the hypophosphite, or if too much of the latter is added to the mercury nitrate, as in either case the double salt is at once decomposed.

Since the formation of the salt from mercuric nitrate necessarily involves the oxidation and waste of much of the hypophosphite, and also yields a mother liquor which acts strongly on the precipitate, mercurous nitrate should be used; moreover potassium hypophosphite is preferable to the barium salt, as with the latter the precipitate is liable to contain barium, apparently as nitrate.

The solution of mercurous nitrate, free from nitrous acid, is best prepared by dissolving mercuric oxide to saturation in nitric acid, and then shaking the solution violently with metallic mercury for a few minutes; in this way, the mercuric salt is quickly and completely changed to mercurous salt.

As the white precipitate obtained on adding potassium hypophosphite to an excess of mercurous nitrate is slowly decomposed when left in contact with the mother liquor, it must be quickly collected and drained on a tile, without previous washing. The *mercurous nitrate hypophosphite* thus obtained is unstable when moist, although when dry it decomposes but slowly, becoming grey in the course of time. It is a white, micaceous powder, slightly soluble in water, by which it is soon decomposed with separation of mercury. Its composition is expressed by the formula $HgH_2PO_2,HgNO_3,H_2O$; it loses its water of crystallisation in a vacuum desiccator, but undergoes scarcely any decomposition, even when kept for some time. When heated, it turns grey above 90°, and explodes a little above 100°, yielding mercury and nitrous vapours; it also explodes if touched with a hot wire.

With hydrochloric acid, it first gives mercurous chloride and then metallic mercury, whilst hot, strong, nitric acid dissolves it completely with escape of nitrous fumes. Sodium chloride converts it into mercurous chloride and sodium hypophosphite, which only very slowly react, yielding metallic mercury. Potassium hydroxide blackens it probably from formation of mercurous oxide.

The mercury and phosphorus in the salt were determined by dissolving it in nitric acid, evaporating to dryness, dissolving in hydrochloric acid, and precipitating the mercury by hydrogen sulphide, and the phosphoric acid by magnesia mixture. The mercuric sulphide was freed from any sulphur precipitated along with it, and dried at 105—110°. The nitric acid was estimated by treating the salt with strong sulphuric acid in Lunge's nitrometer. Loss of weight in the desiccator served for the water determination. The analytical results which follow refer to three separate preparations of the salt.

		Found.		
	Calculated.	I.	II.	III.
Mercury	73·39	73·35	73·01	73·04
Nitrogen	2·59	2·78	2·76	2·82
Phosphorus........	5·68	5·56	5·25	5·50
Water	3·30	3·01	2·45	—

This salt is of interest as a double salt of univalent or quasi-univalent mercury, since it points to the mercurous salts being salts of the radicle $(Hg_2)''$ rather than of Hg'.

A salt has been described by H. Rose (*Ann. Phys. Chem.*, 1837, **40**, 75) as produced by the action between mercuric nitrate and phosphine, and to which he assigned the formula

$$P_2Hg_3'',3[Hg''(NO_3)_2Hg''O].$$

This explosive substance* would seem to be related to the salt I have described, for it is not remote in composition from

$$3Hg'NO_3,Hg'H_2PO_2,$$

and is more probably a mercurous than a mercuric salt.

Bismuth Hypophosphite.

This salt has not hitherto been described. It may be prepared by mixing a solution of bismuth nitrate, free from any unnecessary excess of nitric acid, with barium or potassium hypophosphite, avoiding excess of bismuth nitrate, as the salt is soluble in it. The bismuth hypophosphite, which is precipitated as a white crystalline powder, slowly decomposes in contact with the mother liquor, but, if collected at once and dried on a porous tile, it can be preserved for days unchanged.

The analysis of this salt was carried out much in the same way as that of the mercury salt, except that the bismuth sulphide was dissolved in nitric acid and the solution precipitated by ammonium carbonate as usual. Water was determined as loss in the vacuum desiccator. In the following table the calculation is for

$$Bi(H_2PO_2)_3,H_2O,$$

which therefore expresses the composition of the salt.

		Found.		
	Calculated.	I.	II.	III.
Bismuth	49·41	49·49	49·49	48·77
Phosphorus......	22·09	21·67	21·34	21·19
Water	4·29	3·11	3·26	3·39

Bismuth hypophosphite decomposes very readily when heated, becoming black and giving off phosphine at temperatures only a little above 100°. At a stronger heat, metallic globules and bismuth phosphate are obtained. The globules consist of metallic bismuth free from phosphorus. As about two-thirds of the bismuth is obtained as metal, the decomposition of the bismuth hypophosphite by heat may be expressed by the equation—

$$3Bi(H_2PO_2)_3 = 2Bi + Bi(PO_3)_3 + 6P + 9OH_2.$$

This hypophosphite is noticeable for yielding metal instead of phosphide, but this fact is in accordance with the observation of Berzelius, that bismuth phosphide completely decomposes when heated.

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* It was again examined by Aschan in 1885 (*Chem. Zeit.*), but not quantitatively.

XXVII.—*Kamala.* Part II.

By A. G. Perkin, F.R.S.E.

In a previous communication on this subject (Trans., 1893, **63**, 975), the various constituents of this drug were described, an account being at the same time given of a preliminary investigation of the action of various agents on them. The continuation of this work has consisted chiefly in the study of rottlerin, the principal crystalline constituent of kamala, but progress has been exceedingly slow, as the products formed from it are difficult to obtain in a crystalline condition. Owing to the appearance of a paper on Kamala, by P. Bartolotti (*Gazzetta*, 1894, **24**, i, 1), it was thought advisable to lay before the Society the results which have so far been obtained, especially as it is probable that the detailed investigation will occupy a considerable period of time.

Action of Nitric acid on Rottlerin.

As was mentioned in the previous paper, rottlerin, when treated with nitric acid (sp. gr. 1·5), yields small quantities of three colourless acids, which melt respectively at 282°, 226°, and 232°. Although these acids were specially tested for nitrogen with a negative result, this is now found to be incorrect; the error has probably arisen partly from the very minute quantities that could be spared for this purpose, and from the ease with which they sublime. Experiments performed with much larger quantities have since shown that all these acids contain nitrogen. Fortunately this does not interfere with the value of the analytical results previously obtained, which have been confirmed, and several of which are here again utilised.

Since the previous communication, a fourth substance has been obtained from the mixture from which these acids are isolated, and some slight alteration has been made in the method of working, so that the process is again briefly described here. Finely-powdered rottlerin is added to well-cooled nitric acid (sp. gr. 1·5), in which it dissolves, until some quantity of a colourless crystalline product has separated from the solution. It is then mixed with its own volume of glacial acetic acid, the crystals rapidly collected on glass wool with the aid of the pump, the residue washed with glacial acetic acid, and purified by two or three crystallisations from alcohol.

0·1090 gave 7 c.c. moist nitrogen at 19° and 752 mm. N = 7·30.
0·1176 „ 0·2425 CO_2 and 0·0410 H_2O. C = 56·23. H = 3·87.
$C_9H_7NO_4$ requires C = 55·96; H = 3·59; N = 7·25 per cent.

An analysis of the silver salt gave

*$C = 35{\cdot}69$; $H = 2{\cdot}11$; $Ag = 36{\cdot}51$ per cent.

$C_9H_6NO_4Ag$ requires $C = 36$; $H = 2$; $Ag = 36$ per cent.

To further corroborate this result, a portion of the acid was converted into its methylic salt by saturating a mixture of the acid and methylic alcohol with hydrogen chloride; the clear solution thus formed, after a time, deposited slender, colourless, fine needles; these were collected, washed, recrystallised from alcohol, and analysed, with the following result.

0·1095 gave 0·2341 CO_2 and 0·0447 H_2O. $C = 58{\cdot}30$; $H = 4{\cdot}53$.

0·1185 „ 7·1 c.c. moist nitrogen at 18° and 766 mm. $N = 7{\cdot}01$.

$C_9H_6NO_4{\cdot}CH_3$ requires $C = 57{\cdot}97$; $H = 4{\cdot}34$; $N = 6{\cdot}76$ per cent.

It melted at 158·5°.

The *ethyl salt*, prepared in a similar way, formed colourless needles melting at 138°, and readily soluble in alcohol.

The acid melting at 282° is, therefore, identical with *paranitrocinnamic acid*, the melting point of which is given as 286°. Further proof of their identity was also afforded by a comparison of the acid from rottlerin with that prepared from cinnamic acid, and of their methylic and ethylic salts.

As previously found, the alcoholic mother liquors obtained during the purification of the preceding acid contained the more soluble acid melting at 226°. On analysis, it gave the following numbers.

0·0897 gave 5·4 c.c. moist nitrogen at 19° and 766 mm. $N = 6{\cdot}97$;
*$C = 56{\cdot}02$; $H = 4{\cdot}09$ per cent.

$C_9H_7NO_4$ requires $C = 55{\cdot}96$; $H = 3{\cdot}62$; $N = 7{\cdot}25$ per cent.

As was to be expected, this acid is evidently *orthonitrocinnamic acid*, a fact further borne out by its comparison with the acid prepared from cinnamic acid. That it could not be considered quite free from the para-acid is shown by its melting point 226° (orthonitrocinnamic acid melts at 237°; Tiemann and Oppermann, *Ber.*, 1880, **13**, 2060), and this is readily accounted for by the well-known difficulty of separating these acids by crystallisation. As the total quantity of the ortho-acid yet obtained has not been quite 0·3 gram, its further purification by transformation into its methylic ether was not practicable.

The nitric acid filtrate obtained during the preparation of the two acids just described was poured into water, and the resulting viscous precipitate collected and extracted with ether. The ethereal solution, after agitation with dilute ammonia, was evaporated to dryness, and the oily residue, which had a strong odour of benzaldehyde, was distilled with steam, when a considerable portion passed over as a colourless oil. The distillate was shaken with ether, and the ethereal solution evaporated; the oily residue, on being allowed to stand for some hours, deposited crystals, which were collected and placed upon a porous plate. They melted at 105°, and, when heated, emitted a strong odour of benzaldehyde; obviously they consisted of *paranitrobenzaldehyde.*

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* The analyses marked with an asterisk in this paper have been given in Part I (*loc. cit.*).

The third acid, melting at 232°, was obtained by the action of boiling nitric acid (sp. gr. 1·5) on rottlerin, on the resins of high and low melting point, and on isorottlerin, as described in the previous paper. On analysis, the following numbers were obtained.

0·0781 gave 5·8 c.c. moist nitrogen at 18° and 752 mm. N = 8·48.
*0·1003 „ 0·1845 CO_2 and 0·0318 H_2O. C = 50·16; H = 3·52.
*0·1083 „ 0·1992 CO_2 „ 0·0345 H_2O. C = 50·16; H = 3·53.
$C_7H_5NO_4$ requires C = 50·29; H = 3; N = 8·38 per cent.

An analysis of its silver salt gave the following numbers.

*0·1869 gave 0·2066 CO_2 and 0·0294 H_2O. C = 30·14; H = 1·74.
$C_7H_4NO_4Ag$ requires C = 30·65; H = 1·46 per cent.

To further corroborate this result, a portion of the acid was converted into its methylic salt by treating its solution in methylic alcohol with hydrogen chloride; after a lapse of 24 hours, hot water was added to the solution, and the crystalline mass which separated on standing was collected, washed, and recrystallised from dilute alcohol.

0·1665 gave 11·5 c.c. moist nitrogen at 20° and 761 mm. N = 7·91.
$C_7H_4NO_4{\cdot}CH_3$ requires N = 7·73 per cent.

It formed a glistening mass of colourless needles melting at 96°.

These results show that this acid is *paranitrobenzoic acid*, and this was corroborated by comparison with the acid prepared in the usual manner. The formation of this acid from rottlerin by the action of boiling nitric acid is evidently due to the oxidation of the paranitrocinnamic acid first formed, and the same is probably true of its formation from the other constituents of kamala. It has been already pointed out (*loc. cit.*) that when the acid melting at 282° (now shown to be paranitrocinnamic acid) was treated with boiling nitric acid (sp. gr. 1·5) it yielded the acid melting at 232° (paranitrobenzoic acid); as no metanitrobenzoic acid has been detected among the products of the action of nitric acid on rottlerin, it is evident that the paranitrobenzoic acid has not been formed by the nitration of benzoic acid. Besides oxalic acid previously found, small quantities of other products are present, which, as yet, have resisted all attempts at purification, and among which orthonitrobenzoic acid should be found.

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* The analyses marked with an asterisk in this paper have been given in Part I (*loc. cit.*).

The formation of benzoic and acetic acids when rottlerin is fused with caustic potash, and the production of the same substances from rottlerin and the resin of low melting point by oxidation with hydrogen peroxide in alkaline solution are thus explained, being due to the splitting-up of the cinnamic acid group or groups present in these substances.

The Yellow, Crystalline Colouring Matter.

The properties of this substance have already been described (*loc. cit.*), but at that time enough could not be obtained to make an analysis. However, during the preparation of the rottlerin necessary for carrying out the experiments described in this paper, 0·15 gram was obtained, and, after being purified by recrystallisation from carbon bisulphide, was analysed.

0·0865 gave 0·2165 CO_2 and 0·0478 H_2O. C = 68·26; H = 6·14.
$C_{33}H_{36}O_9$ requires C = 68·75; H = 6·25 per cent.

It appears, therefore, to contain 6H more than rottlerin, and is possibly a reduction product of this substance. It is extremely doubtful if sufficient can be obtained from kamala for a determination of its nature, though it may possibly be obtained from rottlerin during the study of this substance. It is at present proposed to name it *homorottlerin*.

Molecular Weight of Rottlerin.

It was previously shown that, though analyses of rottlerin agreed with the formula $C_{11}H_{10}O_3$, a molecular weight determination gave results considerably higher than those required by this formula. It was, however, difficult to obtain a trustworthy result, owing partly to the very slight solubility of rottlerin in suitable solvents and to the fact that its solutions appear to gradually decompose on long boiling. Attention was therefore directed to the formation of some mono-substitution derivative, the analysis of which would indicate the molecular weight, and this was ultimately effected by the preparation of several metallic derivatives of rottlerin.

Sodium Rottlerin, $C_{33}H_{29}O_9Na$.—If finely-powdered rottlerin is shaken with a cold, aqueous solution containing twice its weight of sodium carbonate (in which it is insoluble), and the mixture cautiously heated on the sand bath to a temperature of about 60°, the suspended rottlerin, without apparently going into solution, gradually assumes a different crystalline appearance, and that some change has taken place is evident from the fact that the product readily dissolves in cold alcohol, whereas rottlerin is insoluble. The crystals were collected, washed with water, allowed to dry at the ordinary temperature, and examined, when they were found to contain sodium, and on treatment with an acid they yielded rottlerin; evidently, therefore, this substance is a sodium derivative. As the preparation of sodium rottlerin in a pure condition by this method is exceedingly difficult and uncertain, other methods were tried. The best is as follows:—5 grams of finely-powdered rottlerin are shaken up with a solution of 10 grams of sodium carbonate in 100 c.c. of water, and 75 c.c. of pure methylic alcohol is added; a clear, orange-brown solution is at once obtained, which, if necessary, is rapidly filtered through calico, and then treated with 100 c.c. of water. If crystallisation does not rapidly ensue, a crystal of sodium rottlerin previously obtained is added, or crystals obtained by further diluting a small portion of the alcoholic solution. Small, glistening leaflets then quickly separate, causing the mixture to have a golden appearance. The product is collected, washed with water, well drained, and dried over sulphuric acid. In the preparation of this and the potassium salt, the operations were carried out rapidly, as prolonged contact with the alkali carbonate causes decomposition. The sodium salt (dried over sulphuric acid) does not lose weight when heated at 110°. The sodium in the salt dried at 110° was determined by incinerating it and treating the residue with sulphuric acid.

0·4400 gave 0·051 Na_2SO_4. Na = 3·82.
0·3333 „ 0 0388 „ Na = 3·77.
$C_{33}H_{29}O_9Na,H_2O$ requires Na = 3·77 per cent.

When dried at 150°, the salt loses a molecule of water of crystallisation, as the following determination shows.

0·6730 gram dried at 150° lost 0·0220 gram, or 3·27 per cent. H_2O.
$C_{33}H_{29}O_9Na.H_2O$ requires 2·95 per cent. H_2O.
0·6510 gram, when incinerated with sulphuric acid, yielded 0·08 Na_2SO_4. Na = 3·97.
$C_{33}H_{29}O_9Na$ requires Na = 3·88 per cent.

Sodium rottlerin forms an orange-brown mass of glistening leaflets, much surpassing in beauty rottlerin itself. It is insoluble in cold water, but when the mixture is heated, it gradually dissolves, and, on continued boiling, is decomposed, with formation of a dirty yellow precipitate. It is readily soluble in ether and in alcohol. Heated at 170—180°, it slowly decomposes, and, when destructively distilled, it behaves similarly to rottlerin.

Potassium rottlerin. $C_{33}H_{29}O_9K$, was prepared by the action of potassium carbonate on rottlerin, the method employed being similar to that used in the case of the sodium salt. It does not lose weight when dried at 110°.

When heated at 170°, it loses 1 mol. of water of crystallisation. 0·686 heated at 170° lost 0·0205. $H_2O = 2·98$.

0·5575 heated at 170° lost 0·0160. $H_2O = 2·87$.

$C_{33}H_{29}O_9K,H_2O$ requires $H_2O = 2·87$ per cent.

0·5415 dried at 170° yielded 0 0780 K_2SO_4. $K = 6·45$.

$C_{33}H_{29}O_9K$ requires $K = 6·41$ per cent.

In appearance and general properties it closely resembles the sodium salt, with the exception that it is more stable, and is not so rapidly decomposed when boiled with water.

The ammonium salt of rottlerin could not be prepared by means of dilute alcohol and ammonium carbonate, but, on adding ammonium chloride solution to the potassium or sodium salts of rottlerin dissolved in dilute alcohol, a small quantity of a crystalline powder was obtained which appears to consist of this salt.

Barium Rottlerin, $(C_{33}H_{29}O_9)_2Ba$.—This was prepared by adding a barium chloride solution drop by drop to a solution of the sodium salt in dilute methylic alcohol, (2MeOH : $1H_2O$), until slightly turbid. On standing, the compound gradually separated as a crystalline precipitate, which was collected, washed with water, and dried over sulphuric acid. It does not lose weight when heated at 110°, but at 150° it apparently gives off 2 mols. of water; the quantity available, however, was too small for an accurate determination.

0·2820 dried at 150° yielded 0·0505 $BaSO_4$. $Ba = 10·53$.

$(C_{33}H_{29}O_9)_2Ba$ requires $Ba = 10·74$ per cent.

This barium salt is a reddish-brown, glistening powder consisting of small prisms; it is insoluble in water, readily soluble in alcohol, moderately so in ether. When boiled with water, it does not appear to decompose. The preparation of this salt in quantity in a crystalline condition is a matter of some difficulty, and requires some practice, as it more readily separates in a resinous condition.

This is even more apparent in the case of *strontium rottlerin,* $(C_{33}H_{29}O_9)_2Sr$, and *calcium rottlerin,* $(C_{33}H_{29}O_9)_2Ca$, both of which, like the barium salt, can be obtained by double decomposition from sodium rottlerin. In appearance they closely resemble the barium compound.

Lead rottlerin, $(C_{33}H_{29}O_9)_2Pb$, is readily obtained by the addition of an aqueous solution of lead acetate to sodium rottlerin in alcohol. An orange-yellow precipitate is thus formed, which is washed with water and dried.

0·8045 dried at 110° gave 0·1790 $PbSO_4$. Pb = 15·19

$(C_{33}H_{29}O_9)_2Pb$ requires Pb = 15·39 per cent.

If an alcoholic solution of lead acetate is added to an alcoholic solution of sodium rottlerin, the lead salt is deposited in groups of fine needles. It is insoluble in water, moderately soluble in alcohol.

Silver Rottlerin, $C_{33}H_{29}O_9Ag$.—If a solution of the sodium salt in methylic alcohol is mixed with a solution of silver nitrate in 50 per cent. methylic alcohol, a crystalline precipitate quickly separates, which, when examined under the microscope, is seen to consist of fine, hair-like needles; but, as the compound formed in this way always contains reduced silver, it is better to prepare it by adding aqueous silver nitrate solution to an alcoholic solution of the sodium salt; the finely-divided canary-yellow precipitate which separates, when examined under the microscope, will be seen to consist of warty nodules; it is collected, washed with water, and dried. It does not lose weight when heated at 150°.

0·5132 dried at 110° on ignition yielded 0·0807 Ag. Ag = 15·72.

0·3735 „ 150° „ „ 0·0600 Ag. Ag = 16·07.

$C_{33}H_{29}O_9Ag$ requires Ag = 15·95 per cent.

Silver rottlerin is moderately soluble in cold alcohol, insoluble in cold water, but is decomposed when boiled with it, with deposition of metallic silver. With hydrochloric acid, it yielded rottlerin and silver chloride.

An *aluminium* compound of rottlerin is readily obtained as an ochre-coloured, amorphous mass on adding alum solution to an alcoholic solution of the sodium salt, whilst ferric chloride in like manner yields a greyish precipitate. Both these precipitates are decomposed by boiling sodium carbonate solution.

The foregoing results show that the formula of rottlerin is $C_{33}H_{30}O_9$, or three times the formula $C_{11}H_{10}O_3$ originally assigned to it, its molecular weight being consequently 566.

The ready production of the above derivatives of rottlerin by the substitution of one hydrogen for a metal, and more especially the fact that the sodium and potassium salts are formed by the action of carbonates in the cold, suggests that rottlerin may be a monobasic acid of the formula $C_{32}H_{29}O_7\cdot COOH$.

In the previous communication (Trans., 1893, **63**, 975), it was shown that rottlerin, when acted on by boiling acetic anhydride, yielded a product, the analyses of which agreed well with the formula $C_{11}H_8O_3(C_2H_3O)_2$, which, when adapted to the new formula, would represent *hexacetylrottlerin*, and that the constitution assigned to this substance is correct, appears to be proved by the existence of a benzoyl compound, $C_{11}H_8O_3(C_7H_5O)_2$, which will be *hexabenzoylrottlerin*, P. Bartolotti (*Gazzetta*, 1894, **24**, i, 1).

Experiments will be instituted with the hope of determining the true formula of the other principal constituents of kamala, namely, isorottlerin, and the resins of high and low melting point, which being allied to rottlerin will no doubt have a correspondingly high molecular weight.

Action of Sodium Carbonate on Rottlerin.

Rottlerin, when boiled with solutions of the alkali hydrates, undergoes decomposition, an odour of benzaldehyde being emitted, and an uninviting resinous substance produced. As the action of the alkali carbonates although similar is less energetic, it was decided to study it; the results at present obtained, however, have been somewhat disappointing, as the decomposition is evidently of a complex nature, and although evidence has been obtained of the formation of at least four substances, yet, from their resinous nature, only one has so far been obtained in a crystalline condition.

In this experiment, 10 grams of finely-powdered* rottlerin were shaken up with a solution of 20 grams of sodium carbonate in 500 c.c. of water, and the mixture gradually heated on the sand bath; as previously mentioned, the first product of the action is sodium rottlerin, which forms at about 60°. When the temperature was raised to 90°, the suspended crystalline product became redder and more granular, and on boiling for a few minutes became slightly sticky. It was then collected upon calico, washed, suspended in water, treated with hydrochloric acid, and the mixture extracted with ether. The ethereal solution, when evaporated to a small bulk and cooled, gradually deposited a crystalline substance, which was collected, washed with a little ether, and purified by crystallisation from ethylic acetate with the aid of animal charcoal. On analysis, it gave the following numbers.

0·1200 gave 0·3261 CO_2 and 0·059 H_2O. C = 74·11; H = 5·46.
0·1105 „ 0·3005 „ 0·056 „ C = 74·16; H = 5·62.
0·1082 „ 0·2922 „ 0·055 „ C = 73·65; H = 5·64.
$C_{29}H_{26}O_6$ requires C = 74; H = 5·53 per cent.

This formula must be regarded as provisional only until some means can be found of obtaining the molecular weight of the substance. Thus obtained, it is a garnet-red, glistening mass of fine, irregular prisms, somewhat resembling rottlerin in appearance, and as it is apparently closely allied to the latter, I propose for it the name *rottlerone*. That it cannot consist of an impure rottlerin (C 69·32, H 5·26) is shown by its insolubility in aqueous solutions of the alkali hydrates even when boiled with them, although, like rottlerin, it is decomposed and resinified by this treatment. It is readily soluble in dilute alcoholic solutions of the alkali hydrates Larger quantities of the substance are being prepared, and its investigation continued.

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* The rottlerin used in these experiments was obtained by the purification of *kamalin*, a crude rottlerin prepared by Merck of Darmstadt.

A Dyeing Property of Rottlerin.

The method of dyeing with kamala is not well understood, and is certainly rather remarkable, for, as previously shown, the various constituents it contains are insoluble in water. It is not intended to enter into the details of the process here, but the method essentially consists in boiling the material (chiefly silk) with kamala suspended in sodium carbonate solution. It is probable that in the process rottlerin plays the chief, if not the only, part, and the result obtained is due, not to the fixing of rottlerin on the material, but of the decomposition products produced by the action of the sodium carbonate, one of which, as shown above, is rottlerone. Even if the material be previously mordanted, no compound of rottlerin can be fixed in the fibre, because, as already stated, the alumina and iron compounds of rottlerin are decomposed by boiling sodium carbonate solution Though of no practical value, it appeared interesting to test the behaviour of sodium and potassium rottlerin towards mordanted calico. For this purpose, they were suspended in water, dissolved by the addition of a little alcohol, the mordanted calico entered, and the whole brought to the boil. As was expected, the material was found to be dyed, yielding the following somewhat poor shades: iron mordant, brownish-black; alumina, pale orange-red; and mixed alumina and iron, orange-brown.

I have received a private communication from Professor Schär, M.D., of Strassburg University, with reference to the "wars" or "wurrus" mentioned in the previous communication, in which he states that the absorption spectra of alkaline alcoholic extracts of this drug and kamala are indistinguishable. He is of opinion, from this fact and their closely allied medicinal properties, that their constituents will be identical or bear a close chemical relationship. Owing to the extreme difficulty of obtaining this substance, its examination has had to be postponed, although, through the aid of the Imperial Institute, I hope shortly to procure some of it.

Clothworkers' Research Laboratory,
Dyeing Department, Yorkshire College.

XXVIII.—*Remarkable Molecular Change in a Silver Amalgam.*

By Fannie T. Littleton.

My attention was directed by Dr. Mallet, of the University of Virginia, to a curious swelling up, apparently attended with escape of gas, exhibited by a specimen of silver amalgam, when it was moderately heated over a lamp. The following experiments were made to determine, if possible, the nature of the change which takes place.

It was first ascertained by analysis that the amalgam originally used consisted of about 15 per cent. of silver and 85 per cent. of mercury. Having prepared a fresh specimen with the same proportions, but using both metals in a carefully purified state, it was found that this new material behaved in the same way as the old, so that the phenomenon did not depend on any foreign metals or other impurities which might have been present in the former specimen. In all subsequent experiments, the mercury used had been recently distilled with care in a vacuum, and the silver was brought to a pulverulent condition by dissolving chemically pure metal ("proof" silver from the United States Mint at Philadelphia) in pure nitric acid, precipitating as chloride, reducing the fresh precipitate by means of an ingot of very pure zinc, washing thoroughly first with dilute hydrochloric acid, and finally with water, and drying at a gentle heat.

When the proportions already mentioned were used, and the mercury was simply poured over the pulverulent silver, union took place at once, with very notable rise of temperature, so that any considerable mass of the amalgam became painfully hot to the hand. The product, when rubbed in a porcelain mortar, became a perfectly homogeneous, pasty mass. When this mass was shaken vigorously in a stoppered bottle, as also when rubbing in the mortar was continued, a small quantity of a black powder appeared upon the surface, sometimes rising in a dust-like cloud when the stopper was removed from the bottle. On heating it over a lamp, the amalgam showed very notable increase of volume, and the surface appeared as if a gas were being given off. After cooling, the amalgam retained its increased volume, was hard and crystalline in structure, a contrast to its former soft, pasty condition, and, on being broken across, was visibly porous throughout.

To ascertain with what proportions of mercury and silver the swelling would be greatest, a rough estimate was made by heating several amalgams of different composition in glass tubes closed at one end, marking on each tube the original volume and the increased volume after heating. The following results were obtained.

	Silver.	Mercury.	Expansion.
I	7·5	92·5	about 8 per cent.
II	15·0	85·0	„ 23⅓ „
III	18·0	82·0	very slight.

Varying the proportions so as to represent the atomic ratio $AgHg_4$, it was found that

Silver.	Mercury.	Expansion
11·87	88·13	gave about 33⅓ per cent.,

which seemed to be the maximum attainable. This amalgam, $AgHg_4$, was used in all the remaining experiments. With it, the rise of temperature, on pouring the mercury over the pulverulent silver, and rapidly shaking the two together in a stout glass bottle of about ¼-litre capacity, was, for a specimen of amalgam, weighing 220 grams, 40° C., namely, from 25° to 65°. A second and more carefully made experiment gave for 156·64 grams a rise from 28·2° to 66·4° = 38·2°. The amount of heat evolved in the act of combination was not, however, determined in a calorimeter.

The black powder which has been mentioned was examined. It was removed by means of a camel's hair pencil from the surface of the amalgam and of the bottle in which the latter had been shaken up, care being taken to reject all such minute globules of mercury as could be seen with the aid of a hand lens. The powder was digested with strong acetic acid, to dissolve any mercurous oxide which might be present, and, after filtration, the liquid was tested with a bit of copper wire, gently warming for some time, and adding a drop of hydrochloric acid; the copper became slightly coated, and, after drying, it gave, on being heated in a miniature glass tube, minute globules of mercury visible with a lens. The part of the powder undissolved by acetic acid was dried and heated in another small tube; it also gave a sublimate of mercury globules, and left a residue which, on being dissolved in a drop of nitric acid and precipitated by hydrochloric acid, gave chloride of silver, easily soluble in ammonia. Hence the black powder seems to consist of both metals in a state of fine subdivision, with a part of the mercury converted into mercurous oxide.

To determine more closely the amount of expansion, the sp. gr. of the amalgam under different conditions was examined, using large masses (50—80 grams), but weighing accurately on a good analytical balance.

I. The amalgam, $AgHg_4$, in its original soft and pasty state, as produced by rubbing the silver and mercury together in a mortar until the mass was entirely homogeneous, had the density 13·340 at about 24°/24°. The calculated density for this temperature, assuming no change of volume as the result of union between the metals, is about 13·216, so that some little contraction is indicated.

II. The density of the same amalgam after remaining at atmospheric temperature, about 22—27°, for several days was found to be 13·412. It was slightly crystalline, and harder than at first, but could be easily crushed between the fingers.

III. Two specimens of the amalgam, $AgHg_4$, which had been heated (in a Sprengel vacuum), had swelled up and become quite crystalline, brittle, and too hard to be readily crushed in the fingers, after cooling to atmospheric temperature, gave $d = 9·229$ and 9·119 respectively. They were very porous, full of small cavities, so much so that it was not possible to avoid water entering the pores to some extent from the surface, and hence the sp. gr. of the porous mass as a whole could not be taken with great accuracy, but the approximate values thus found indicate the large increase of bulk resulting from the heating. When crushed in a mortar and rubbed sufficiently, this crystalline and swollen amalgam could be brought back to its original soft and pasty state.

The swelling up began at a temperature of about 240°, and continued until an immersed thermometer indicated 335°; the phenomenon seemed to be most marked at about 315° to 320°.

The appearance so closely resembled that of an escape of gas from the material heated, that the experiment, originally tried in the air, was repeated more than once in a vessel, made from Bohemian glass combustion tubing of large size, connected with a Sprengel pump, and well exhausted in advance of the heating. In a first attempt to collect any gas given off, 105·52 grams of amalgam consisting of 12 per cent. of silver and 88 per cent. of mercury, seemed to swell up more notably in the exhausted vessel than if heat had been applied under atmospheric pressure, but only a small bubble of gas was given off and collected. It proved to be oxygen, and probably came from some slight admixture of the black powder already mentioned. In another experiment, the amalgam $AgHg_4$ was used, and on heating 253·74 grams in a vacuum, a quantity of gas was obtained which would measure 1·62 c.c. at normal temperature and pressure (0° and 760 mm.); this also proved to be oxygen. It had been imagined as possible that silver in solution in mercury at common temperature might absorb gaseous oxygen as the former metal in the molten condition does, and might give it up on moderate heating, but it seems evident that this does not take place, at any rate to any considerable extent, and is not the cause of the phenomenon under examination, which must be ascribed to molecular change involving only the two metals.

The marked development of heat which attended the union of the silver and mercury was suggestive of analogy to the similar but more striking effect of bringing together mercury and either of the alkali metals, and, therefore, sodium amalgam was prepared in pasty form, and heated, with the result that a similar swelling-up took place, though to a less extent than in the case of silver amalgam, and a similar hardening and assumption of crystalline structure appeared after cooling. Pasty copper amalgam was also tried, and showed something like the same behaviour, but the mass took a longer time to cool and settle to the crystalline state, and was not so porous as the amalgam of silver in the same condition.

This similarity of behaviour of silver to sodium and to copper in relation to mercury serves but to supply another bit of evidence in support of the positions assigned to the first three metals in classification based on the "periodic law."

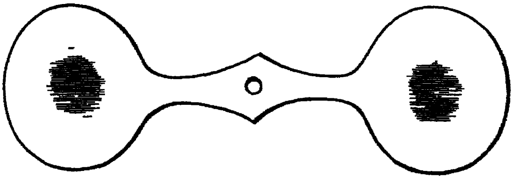
XXIX.—*Chemical Composition of two Silver Ornaments from Inca Graves at Chimbote, Peru.*

By Cora Walker.

A former student in the laboratory of the University of Virginia (U.S.), Mr. J. Lawton Taylor, now a mining engineer at Santa Cruz de Alaya, in Sinaloa, Mexico, was in 1875 engaged in connection with mining work in Peru, and at Chimbote, on the coast, some seventy-five miles southwards from Truxillo, he obtained a number of silver ornaments from Inca graves antecedent in age to the Spanish Conquest. These he afterwards brought back to the United States, and presented several of them to Dr. Mallet. of the University of Virginia. At the suggestion of the latter, I undertook the analysis of two of these ornaments, which are believed to have been worn by the dead persons in whose graves, near Chimbote, they were found. Prescott (*History of the Conquest of Peru*, I, 151, 152), says:—"The royal magazines and the *huacas*, or tombs of the Incas, have been found to contain many specimens of curious and elaborate workmanship. Among these are vases of gold and silver, bracelets, collars, and other ornaments for the person."

One of the two specimens examined, A, consisted of a silver plate, which, when spread out, had the form and dimensions shown in Fig. 1; it was 68 mm. long, with nearly circular ends of about 20 mm. in diameter, which were somewhat concave on one side, and a small perforation in the middle of the length, apparently to afford means of attachment. As received, the plate was bent double near the middle of its length. It weighed 4·099 grams.

FIG. 1.



A. von Humboldt (*Vues des Cordillères et Monuments des Peuples Indigènes de l'Amérique.* Paris, 1810, 87), referring to Plate XIV in that book, says of Figs. 1—4: "*Quatre guerriers mexicains: les trois premiers portent le vêtement appelé* ICHCAHUEPILLI, *sorte de cuirasse de coton qui avait plus de trois centimètres d'épaisseur, et qui couvrait le corps depuis le col jusqu'à la ceinture. Les soldats de Cortez adoptèrent cette armure, qu'ils désignèrent sous le nom d'*ESCAUPIL, *dans lequel on reconnaît à peine un mot de la langue aztèque. L'*ICHCAHUEPILLI *résistait parfaitement aux flèches.*" Round the lower border of this cotton cuirasse in each of the three figures appears a row of ornaments of the form of the Inca silver specimen examined.

The other ornament, B, was a ring, made of a flat band of silver, which, when cut across and straightened out, was 65·5 mm. long and 9·7 mm. wide, and weighed 2·4265 grams. As received, it was crumpled, and prosented the appearance of Fig. 2.

FIG. 2.

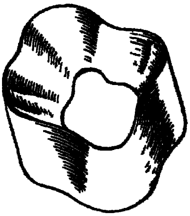
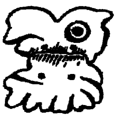


FIG. 3.



Belonging to this ring, but detached from it, was a small ornament rudely carved from the mother-of-pearl inner side of some shell, apparently intended to represent the head of an aminal. It had four small perforations for attaching it to the ring. Von Humboldt (*Vues des Cordillères*, Plate XXVII) shows hieroglyphic figures of the Mexican calendar much resembling this head in general character.

Before making the analyses, both ornaments were gently and carefully washed with water, to remove any particles of mere earthy matter adhering to the surface, but not so as to disturb the firmly attached crust which had formed by chemical alteration of the metal beneath; after this cleansing they were dried and weighed.

The crust was then removed by treatment with aqueous solution of ammonia, with exposure for some time to the air. This treatment dissolved the silver chloride and compounds of copper, of which the crust proved to be in large measure composed. The chloride of silver was recovered from the ammoniacal solution by the addition of nitric acid, and the copper was precipitated as cupric oxide by sodium hydroxide. Loosened by the ammonia, but not dissolved, there was a residue of siliceous material (earth and sand), with a very little organic matter.

The metallic portions of the ornaments, thus stripped of incrustation, were then treated with nitric acid, which dissolved nearly the whole. The small residue insoluble in the acid was, after treatment with a few drops of ammonia, ignited, weighed, and cautiously fused before the blowpipe; in each case it yielded a minute globule of gold. The silver was precipitated by hydrochloric acid, and the chloride ignited with the usual precautions and weighed. Lead, which was present only in the ring, was removed by sulphuric acid. Copper was determined as cupric oxide; iron and zinc also as oxides, the last two metals being also found only in the ring.

Of the gross weight of the ornament A, the crust, removed by aqueous ammonia, formed 2·41 per cent. This crust was composed of

Chloride of silver	0·43
Basic carbonate of copper, of a green colour	0 83
Siliceous (and a little organic) matter.....	1·15
	2 41

The quantity of the basic copper carbonate was far too small to allow of its composition being accurately ascertained; from the amount of copper actually determined as cupric oxide, it has been calculated as $Cu_2(HO)_2CO_3$, or malachite. The metallic portion of this ornament consisted of

Ag.	Cu.	Au.	Total.
85·24	13·96	0·15	99·35

In the case of the ring, B, the crust represented 1·52 per cent. of the gross weight. It contained but a trace of silver chloride, and was composed almost entirely of cuprous oxide, with a very little siliceous matter.

The percentage composition of the metallic portion of the ring, taken as a whole, was as follows:

Ag.	Cu.	Au.	Fe.	Zn.	Pb.	Total.
25·51	72·09	0·25	1·21	0·50	0·10	99·66

Notwithstanding the small proportion of silver, the colour of the alloy on the surface was fairly white. The ring was made from a strip of metal by lapping the ends and soldering them together. It was not possible to separate the solder itself, but, in order to form some idea of its composition, the soldered part was cut away from the rest and analysed separately: the constituents found are included in the tabular statement of the composition of the whole ring, given above. All of the lead and zinc, and the greater part of the iron, were found in the soldered part, and may be assumed to have formed part of the solder.

The results of these analyses seem worth recording, as a small contribution to our knowledge of early Peruvian metallurgy. I have seen no reference to the form in which silver was known by the Incas to occur in nature, but the presence in each of these ornaments of a minute amount of gold, the well-known occurrence in the Andes of Peru and Chili of native silver and copper, sometimes in very considerable masses, the easy utilisation of the metals when thus found—while the reduction by furnace methods of the sulphurous ores of silver (or even the chloride and bromide), in their most commonly observed condition of admixture with large proportions of siliceous or calcareous vein-stones, would not be so simple or easy—may perhaps be taken to suggest that these relics of primitive Inca workmanship were made from the native metals simply melted down in the furnaces, of which A. de Herrera (*Historia General de los Hechos de los Castellaños en las Islas y Tierra Firme del Mar Oceano*, Madrid ed., 1726, Decada V, f. 77) has the following notice:—

"*Los Indios se aprovechaban de la Plata, por fundicion en Hornillos, adonde el viento soplase recio, i con Leña, i Carbon: los Castellaños la benefician con Açogue, i es mas provechoso.*"

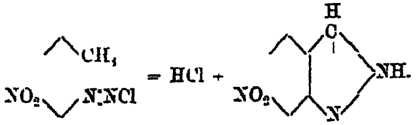
Further on, in the same passage, reference is made to the use of both forced blast ("viento da Fuelles") and natural draught.

The statement that the Spaniards obtained a better yield of silver by using mercury than the "Indians" of Peru by means of their furnace fires was written long after the Conquest. If it be assumed that the native furnace methods referred to had been applied to like natural material in the early days of Inca civilisation, before the arrival of Europeans, this statement would seem to imply that silver *ores*, in the proper sense of the term, were then worked, as well as the native metal.

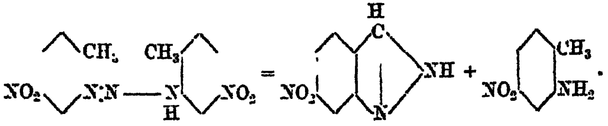
XXX.—*On Some Derivatives of Ethylorthotoluidine.*

By W. MacCallum, jun.*

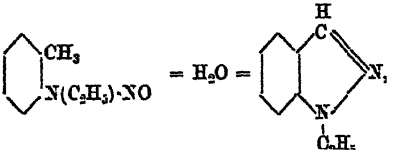
Witt, Noelting, and Grandmougin (*Ber.*, 1890, **23**, 3635) have shown that on boiling the diazo-derivative of nitro-orthotoluidine (m. p. 107°) with water, nitroindazole is formed as well as the cresol, thus



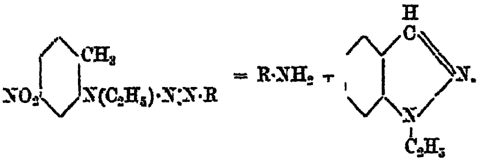
On the other hand, Heusler (*Ber.*, 1891, **24**, 4160) found that on heating with glacial acetic acid the diazoamido-compound prepared from this nitrotoluidine, nitroindazole and nitrotoluidine are produced according to the equation



At the suggestion of Professor Noelting, I have endeavoured to ascertain if nitrosoethyltoluidine and the diazoamido-compounds of nitroethyltoluidine do not in an analogous manner give isindazole derivatives. The former, for example, on losing the elements of water, might give ethylisindazole, thus



whilst the latter might decompose into amine and nitroethylisindazole



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* This work was done by the late W. MacCallum, jun., in the laboratory of the *Chemie Schule* in Mülhausen during the year 1893. Owing to the sad death of this young and promising worker, it is only now published from his notes by his friend Dr. Hepburn.—[E. Noelting.]

My experiments led to negative results, but some new compounds were prepared, and several observations were made which are described in the following pages.

Nitroethylorthotoluidine, [Me : NHEt : NO_2 = 1 : 2 : 4].

Pure orthoethyltoluidine, boiling at 208—209° (uncorr.), was obtained from the nitrosamine. 36 grams of this ethyltoluidine was dissolved in 360 grams of sulphuric acid (96 per cent.), and a mixture of 27 grams of nitric acid (66 per cent.), and 54 grams of ordinary strong sulphuric acid slowly added, the temperature being kept at 2° not only during the operation but also for 12 hours afterwards; the mixture was then poured on to ice, and neutralised with solid sodium carbonate. The precipitated nitro-derivative, weighing 30·5 grams, crystallised from alcohol in light red needles, melting at 81—82°.

0·1973 gave 0·4287 CO_2 and 0·1210 H_2O. C = 59·79; H = 6·81.
0·2440 „ 33·5 c.c. moist nitrogen at 18° and 747·3 mm. N = 15·58.
$C_9H_{12}N_2O_2$ requires C = 60·00; H = 6·66; N = 15·55 per cent.

Ethyltoluylenediamine, [Me : NHEt : NH_2 = 1 : 2 : 4].

This compound was prepared by reducing the above nitro-compound either by tin and hydrochloric acid, or by zinc dust and hydrochloric acid. By the former method, a well-defined crystalline double salt was obtained, whilst the latter method gave a yield of diamine equal to 85 per cent. of the theoretical quantity.

0·129 gave 21·6 c.c. moist nitrogen at 18·6° and 742·6 mm. N = 18·83.
$C_9H_{14}N_2$ requires N = 18·66 per cent.

Ethylmetatoluylenediamine is a colourless liquid which boils at 274—275° (uncorr.), and rapidly becomes brown on exposure to air. It is easily soluble in alcohol, ether, and benzene. It forms salts with acids, which are easily soluble in water. It is converted by diazobenzene chloride into a chrysoïdine, which is a proof that the amido-groups, and, therefore, also the nitro- and amido-groups in the first-described nitro-derivative, are relatively in the meta-position.

Nitroethylacetorthotoluidide, [Me : NEtAc : NO_2 = 1 : 2 : 4].

2·2 grams of metanitroethylorthotoluidine having been dissolved in a small quantity of glacial acetic acid, 1 gram of acetic anhydride was added, and the mixture heated on the sand bath during 12 hours. The product was then poured into water, precipitated with ammonia, crystallised from dilute alcohol and then from benzene by precipitation with light petroleum.

0·23675 gave 27·1 c.c. moist nitrogen at 14° and 7·35 mm. N = 12·99.

$C_{11}H_{14}N_2O_3$ requires N = 12·70 per cent.

Metanitroethylacetorthotoluidide is very soluble in alcohol and benzene, crystallising from the former in white plates, which melt at 90°; it is only sparingly soluble in light petroleum.

Monobromometanitroethylorthotoluidine, [Me : NHEt : NO_2 : Br = 1 : 2 : 4 : ?].

5 grams of metanitroethylorthotoluidine was dissolved in 55 grams of glacial acetic acid, and 5 grams of bromine slowly added. The white crystals of the hydrobromide were collected, washed with glacial acetic acid, and then with absolute alcohol. They melted and decomposed at 194—195°.

0·2522 gave 18·4 c.c. moist nitrogen at 18° and 750 mm. N = 8·3.
0·1755 „ 0·1941 AgBr. Br = 47·06.

$C_9H_{11}N_2O_2Br,HBr$ requires N = 8·28; Br = 47·33 per cent.

On adding the hydrobromide to water, it was converted into the reddish-yellow base, which crystallised from alcohol in needles melting at 114°.

0·2275 gave 21·9 c.c. moist nitrogen at 21° and 744 mm. N = 10·72.
0·2202 gave 0·15818 AgBr. Br = 30·47.

$C_9H_{11}N_2O_2Br$ requires N = 10·77; Br = 30·88 per cent.

Metanitroethylnitroso-orthotoluidine, [Me : NEt·NO : NO_2 = 1 : 2 : 4].

On adding a strong aqueous solution of sodium nitrite slowly to the alcoholic solution of one molecular proportion (1 gram) of metanitroethylorthotoluidine and two molecular proportions of hydrochloric acid, an almost colourless salt at once began to separate, which on treatment with water gave the yellow base; the latter, after crystallisation from alcohol, melted at 56°; yield, 1 gram. Submitted to Liebermann's test for nitroso-compounds, the results were as follows. Strong sulphuric acid and phenol gave a blue-green coloration in the cold, and a blue when heated; the heated mixture poured on to ice gave a brownish-red liquid, which with excess of alkali changed to green (see "Effect of Dehydrating Agents on the Nitrosamine").

0·1191 gave 21·3 c.c. moist nitrogen at 18·5° and 750 mm. N = 20·33.

$C_9H_{11}N_3O_3$ requires N = 20·01 per cent.

Several attempts to convert the nitrosamine into the isomeric nitroso-compound, $C_6H_2(NO_2)(NO)(CH_3)\cdot NH\cdot C_2H_5$ [= 1 : 2 : 4 : 5], by Fischer and Hepp's method (*Ber.*, 1886, **19**, 2991), resulted in the immediate breaking off of the nitroso-group, and the quantitative formation of metanitroethylorthotoluidine, which was identified by its melting point (81—82°).

Effect of Dehydrating Agents on the Nitrosamine.

As already stated, it was thought that the effect of dehydrating agents on metanitroethylnitroso-orthotoluidine might be to remove the elements of water, and so to form an isindazole. The action, however, was not of this nature, but gave rise to metanitroethylorthotoluidine, owing to the elimination of the nitroso-group. The dehydrating agents used were (*a*) strong sulphuric acid, (*b*) zinc chloride, with alcohol as solvent for the nitrosamine, and (*c*) zinc chloride melted with the nitrosamine alone.

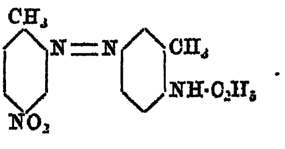
Action of Diazo-compounds on Ethyltoluidine and Nitroethyltoluidine.

1. *Diazotised Orthotoluidine on Paranitroethylorthotoluidine.*—On adding a concentrated, aqueous solution of diazotised orthotoluidine and excess of sodium acetate to ethylorthotoluidine, dissolved in glacial acetic acid, the mixture began to give off nitrogen after a time, and metanitroethylorthotoluidine separated.

An attempt to effect combination by adding an alcoholic solution of diazotised orthotoluidine to an alcoholic solution of the toluidine gave the same result.

2. *Diazotised Paranitro-orthotoluidine on Ethylorthotoluidine.*—3 grams (1 mol.) of paranitro-orthotoluidine was diazotised in aqueous hydrochloric acid solution, and added to 2·7 grams (1 mol.) of ethylorthotoluidine dissolved in glacial acetic acid, to which excess of sodium acetate had been added. The deep red oil, which separated immediately, was extracted with ether, and on distilling off the ether a deep red solid was left, which, after crystallisation from benzene, melted at 154—155°. When the crystallised product was boiled with hydrochloric acid, it seemed as if there were a slight evolution of nitrogen; it was collected, treated with warm sodium hydroxide, and finally recrystallised from alcohol, when it melted at 156°. As, on the addition of diazobenzene chloride to the sodium hydroxide used above, no coloration was obtained, it was concluded that this contained no cresol, and, therefore, also that the product of the action did not contain a diazoamido-compound.

Ethylorthotoluidine coupled with diazotised metanitrotoluidine thus gives an amidoazo-compound directly, whose constitution is, in all probability, represented by the formula



0·1645 gave 28·5 c.c. moist nitrogen at 17° and 723 mm. N = 19·1.
$C_{16}H_{18}N_4O_2$ requires N = 18·78 per cent.

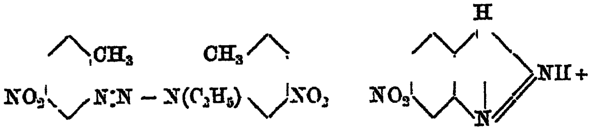
3. *Diazotised Paranitro-orthotoluidine on Paranitroethylorthotoluidine.*—The diazotisation of the nitrotoluidine and the union were effected in the same manner as that described under (2).

The pale yellow diazoamido-compound separated at once, and on crystallisation from alcohol melted at 125°.

0·1855 gave 34·2 c.c. moist nitrogen at 17° and 727 mm. N = 20·44.
$C_{16}H_{17}N_5O_4$ requires N = 20·40 per cent.

Ethyldiazoamidonitrotoluene is soluble in ether and alcohol, and crystallises from the former in long, pale yellow needles melting at 125°. When heated with mineral acids, it is decomposed with evolution of nitrogen; and its alcoholic solution, if left in contact with hydrochloric acid, becomes red, owing to the formation of the corresponding azo-compound.

If submitted to the same treatment as that applied by Heusler (*Ber.*, 1891, **24**, 4160) to diazoamidonitrotoluene, it behaves like the latter, the same nitroindazole being formed as that obtained by Witt, Noelting, and Grandmougin (*Ber.*, 1890, **23**, 3635) on their diazotising metanitrotoluidine and heating it in the presence of dilute sulphuric acid. The action may be represented thus:



$C_6H_3(CH_3)(NO_2){\cdot}NH{\cdot}C_2H_5$.

5 grams of the diazoamido-compound were heated for 1½ hours on the sand bath with 20 grams of glacial acetic acid. The product of the action was passed into water, made alkaline with sodium hydroxide, and the metanitroethylorthotoluidine separated by distillation. The residual oil was treated thrice with boiling water, and the undissolved portion, which solidified on cooling, was crystallised from alcohol; it then melted at 180°, and corresponded in every way with the nitroindazole already mentioned. Yield, 57 per cent. of the theoretical.

0·1479 gave 34·3 c.c. moist nitrogen at 16° and 741·5 mm. N = 25·8.
$C_7H_5N_3O_2$ requires N = 25·7 per cent.

4. *Diazotised Metanitraniline on Paranitroethylorthotoluidine.*—The diazotisation of metanitraniline and the union of the resulting diazo-compound with the toluidine were effected in the same manner as that described under (2). The resulting diazoamido-compound is

easily soluble in alcohol and benzene, and crystallises equally well from ether. It forms yellow crystals which melt at 88°.

0 1985 gave 37·3 c.c. moist nitrogen at 19·5° and 750 mm. N = 21·21
$C_{15}H_{15}N_5O_4$ requires N = 21·27 per cent.

XXXI.—*Acidimetry of Hydrogen Fluoride.*

By TAMEMASA HAGA, F.C.S., Assistant Professor of Chemistry, and YŪKICHI ŌSAKA, Graduate, Imperial University, Japan.

So far as we can find out, the acidimetry of hydrogen fluoride has not yet been particularly investigated, but it is well known that as an acid it stands apart from hydrogen chloride and other strong mineral acids. For whilst it even surpasses sulphuric acid in the intensity of its reaction with water and many organic substances, it yet shows such mild acidic characters, that its "avidity" number places it in this relation among vegetable acids. Further, it not only decomposes the oxides of some metalloïds, such as boron, silicon, phosphorus, and sulphur, forming fluorides possessing some degree of stability in presence of water, but also gives with potash, soda, and ammonia, salts which are alkaline to litmus.

To investigate the subject, we have experimented with the following common indicators of neutralisation of acids by bases; litmus, lacmoïd, methyl-orange, phenacetolin, phenolphthalein, rosolic acid, cochineal, brazil wood, and turmeric paper. These indicators have been prepared and used in the usual way, for the most part as described in Sutton's *Volumetric Analysis*. In order to ascertain what personal difference there might be in the estimation of the particular shades of colour which indicated neutralisation, we worked separately, and on materials all prepared by each for his own use. The first and last of the tables appended contain the results obtained by Haga, and the second those obtained by Ōsaka.

For titration in the experiments recorded in Tables I and II, decinormal solutions, in the experiments given in Table III twice-decinormal solutions of potassium and sodium hydroxides and of ammonia were taken. They were almost pure, containing only the merest traces of silica and alumina, but as these, and also carbon dioxide when present in noticeable quantity, affect the indications of some of the colour reagents, we were careful to determine for each indicator the exact titre of the alkali solutions in terms of a decinormal sulphuric acid which had been standardised by barium chloride, thus rendering ourselves independent of the effects of any impurities present.

The hydrofluoric acid examined was purified in the following way. Commercial, "pure" hydrofluoric acid solution was distilled in a platinum retort after adding a few drops of a saturated solution of potassium permanganate and a little potassium hydroxide. The distillation went on at about 130°, and the product was found to be free from hydrochloric acid and other foreign matters. Silica was sought for by Jörgensen's chloropurpureocobaltic chloride test, and not found. Before purification, the acid gave a small quantity of precipitate when mixed with this reagent and allowed to remain for three days, but the distilled acid gave none after standing for a week.

The purified acid was diluted and preserved for use in a gutta-percha bottle, which had for years been holding the acid before its final purification. For each titration, a portion was weighed off in a platinum crucible with well-fitting lid, and was then washed into a large platinum dish in which the neutralisation was effected, except that in some cases the results recorded in Table I were obtained by transferring the solution, when almost neutral, to a glass vessel, in order to observe the shade of colour more accurately.

The strength of the acid was determined gravimetrically by mixing in a platinum crucible a weighed quantity of the solution with excess of slaked lime freshly made each time from a weighed quantity of precipitated calcium carbonate, allowing the mixture to stand during the night, drying, and then igniting till the weight became constant. The solution of the acid used for the trials recorded in Table I was also assayed by digesting it with precipitated and finely-divided silica, and then igniting with a little sulphuric acid; the results of the two methods agreed well. That used in the trials recorded in Table III was assayed also by gravimetrically estimating the acid as calcium fluoride. The silica method gave in this case a low result, and was rejected.

Litmus as Indicator.—Only historically, and because of the universal employment of litmus for testing neutrality, do we give it the first place in the titration of hydrogen fluoride. On the addition of potash or soda to dilute solutions of hydrofluoric acid coloured by litmus, the red colour rapidly deepens to violet, and by the time one molecule of alkali has been added, the litmus has become almost pure blue, that is, blue almost entirely free from any violet tinge. In fact, the effect on litmus in the saturation of hydrogen fluoride with potassium hydroxide is much like that reversed of the saturation of potassium carbonate by sulphuric acid. However, by practice and by keeping before one a second vessel of water coloured by litmus of the right tint—full blue, as it would be called—it is possible to titrate hydrofluoric acid by means of litmus; its use, however, is not recommended.

Blue litmus paper, reddened with a solution of potassium fluoride containing a small quantity of hydrogen fluoride, becomes blue again when left exposed to the air. If the paper be wetted soon after it has become blue, the red colour will be almost always restored, but if it is allowed to dry thoroughly, subsequent moistening with water generally fails to bring back the red colour. The colouring matter seems to be modified by drying up with the fluoride. Dissolved litmus added to such a solution is also coloured red when much water is present, but becomes more and more blue on evaporating the solution, and when it has become sufficiently concentrated the greater part of the colouring matter separates as a blue powder. This change to blue is not due to loss of hydrofluoric acid, for on adding water the colouring matter dissolves again, giving a red solution as before. A solution in which litmus paper was turned apparently permanently red, and only on drying became neutral or very faintly alkaline, was in one trial found to correspond very nearly to HK_3F_4. Litmus paper is known to be reddened by monopotassium orthophosphate in solution, and to become blue again when dried, from which it may be inferred that hydrogen fluoride, like hydrogen phosphate, is a polybasic acid, H_2F_2, or H_3F_3, or H_4F_4.

Lacmoid solution behaves essentially like litmus, the difference being that much less alkali is required to produce a bluish-violet colour in a solution coloured by lacmoid than in one coloured by litmus. By titrating to a distinct blue, good results may be got with it, but it is not a desirable indicator. Lacmoïd paper behaves like litmus paper.

Phenacetolin changes in colour somewhat gradually when near the neutrality point, but by titrating to pure purple, or rose-violet free from any tinge of yellow, it may be used successfully.

Methyl-orange is quite useless for the ordinary titration of hydrogen fluoride, although it seems to find neutrality in K_2HF_3. The colour changes are very ill-defined.

Phenolphthalein is most satisfactory as an indicator for hydrogen fluoride, giving a very sharp colour change at the point of neutrality. It cannot, of course, be used with ammonia.

Rosolic acid is almost equal to phenolphthalein, but not quite so sharp in its indication. It can be used with ammonia as titrating agent, although ammonia is a little slower than the fixed alkalis in affecting this and other colours. In the case of this indicator, and also of phenolphthalein, the change of colour is well adapted for being observed in platinum vessels.

Cochineal and *brazil wood* behave alike. Both become violet gradually before the acid is neutralised, but the change is ill-defined; finally they turn bluish-violet. This final change of colour is fairly sharp, and is satisfactory for indicating neutrality. Brazil-wood paper becomes bluish-violet before all the acid is neutralised, and is therefore unsuitable for use.

Turmeric paper is satisfactory, but not quite so sensitive as some of the other indicators, and near the finishing point responds slowly.

TABLE I.

Strength of the hydrofluoric acid (*a*) by lime method, 2·79 per cent.; (*b*) by silica method, 2·78 per cent.; mean, 2·785 per cent. Of this solution from 1·2 to 2·9 grams were taken for each determination and titrated with a decinormal solution of the alkali, of which it required from 16 to 39 c.c.

Indicator.	Colour when neutralised.	Acid found in 100 parts of the solution instead of 2·785.		
		With potassium hydroxide.	With sodium hydroxide.	With ammonia.
Rosolic acid	Distinctly red	2·825	2·776	2·84
Phenolphthaleïn	Distinctly pink	2·821	2·790	—
Litmus	Pure litmus blue	2·791	2·802	2·732
Brazil wood	Violet	2·814	2·786	2·805
Phenacetolin	Purple	2·832	2·796	2·765
Lacmoïd	Pure lacmoïd blue	2·809	2·798	2·710

TABLE II.

Strength of the hydrofluoric acid by the lime method (*a*), 6·29 per cent.; (*b*) 6·34 per cent.; (*c*) 6·30 per cent.; mean, 6·32 per cent. Of this solution, from 0·7457 gram to 2·1622 grams were taken for each determination, and titrated with a decinormal solution of the alkali, of which it required from 23·3 to 68·7 c.c.

Indicator.	Colour when neutralised.	Acid found in 100 parts of the solution instead of 6·32.		
		With potassium hydroxide.	With sodium hydroxide.	With ammonia.
Litmus	Distinctly blue	6·47	6·42	6·52
Rosolic acid	Distinctly red	6·31	6·38	6·41
Rosolic acid	Faintly red	—	—	6·35
Phenacetolin	Purple	6·40	6·11	6·33
Phenacetolin	Faintly violet	6·29	5·94	6·22
Phenolphthaleïn	Just pink	6·30	6·37	-
Cochineal	Violet	6·22	6·00	6·30
Cochineal	Faintly violet	6·16	—	6·16
Litmus	Faintly blue	6·28	—	6·29
Lacmoïd	Distinctly blue	6·19	6·00	6·22

TABLE III.

Strength of hydrofluoric acid (*a*) by lime method, 24·93 per cent.; (*b*) by silica method, 23·98 per cent.; (*c*) by calcium fluoride method, 25·11 per cent.; mean of (*a*) and (*c*), 25·02 per cent. Of this solution from 1·488 to 0·7457 grams were taken for each determination and titrated with a twice-decinormal solution of the alkali, of which it required from 93·23 to 45·76 c.c.

Indicator.	Colour when neutralised.	Acid found in 100 parts of the solution instead of 25·02.		
		With potassium hydroxide.	With sodium hydroxide.	With ammonia.
Rosolic acid	Distinctly red...	24·82	24·77	24·96
Phenolphthaleïn ..	Distinctly pink..	25·00	25·00	—
Litmus	Pure litmus blue	24·55	24·60	24·49
Brazil wood	Violet..........	24·71	24·99	24·51
Phenacetolin	Purple.........	24·77	24·85	24·77
Cochineal	Violet	24·86	24·64	24·52
Lacmoid	Pure lacmoid blue	24·50	24·48	24·40
Turmeric paper ...	Reddish-brown..	24·77	25·10	25·05

It will be seen that, as in the case of the ordinary vegetable acids, the best indicator is phenolphthaleïn, or, when ammonia is the titrating agent, rosolic acid.

It should be borne in mind that all these indicators give satisfactory results only when the alkali solution is almost pure. The use of an impure alkali solution, or of a solution which has been kept long enough in glass vessels to have taken up silica, carbonic acid, and other impurities in appreciable quantity, is liable to give results which are ill-defined, and generally too low.

In conclusion, we have to return our thanks to Dr. Divers for his valuable suggestions in working out this paper.

XXXII.—*The Magnetic Rotation of some Unsaturated Hydrocarbons.*

By W. H. PERKIN, Ph.D., F.R.S.

IN connection with the various accounts I have had the honour of bringing before this Society on the magnetic rotation of different compounds, the only measurements of the olefines which have been given are those of amylene. Hitherto, the results obtained have been kept back, in the hope that several other members of this series might be examined, and thus a more complete account of the group given. The difficulty of obtaining additional members of this series, however, and the investigation of other substances, has prevented further progress being made in this direction. Although the number of olefines examined has not been so large or so suitable for comparison as could be wished, the rotations of other hydrocarbons related to them have been measured, and a comparison of these with the olefines is of considerable interest, both in relation to their constitution and also because they are more highly unsaturated. On this account it appeared desirable, without further delay, to give all the results obtained, up to the present, with open chain unsaturated hydrocarbons.

The following is a list of the substances examined.

- Amylene (new specimen).
- Hexylene.
- Octylene.
- Diamylene.
- Diallyl.
- Isoprene.
- Dipropargyl.

Amylene. Trimethylethylene, $(CH_3)_2C{:}CH{\cdot}CH_3$.

Like the previous specimen examined (Trans., 1884, **45**, 449), this was prepared from dimethylethylcarbinyl iodide (most of which distilled at 135°, corr.), by dropping it into boiling alcoholic potash. The trimethylethylene thus obtained, after being well washed with water, dried, and distilled, boiled at 35·5—36·5°, corr. The density determinations gave

d 4°/4° 0·6726. *d* 15°/15° 0·6620.
d 10°/10° 0·6669. *d* 20°/20° 0·6577.
d 25°/25° 0·6535.

The magnetic rotation, twice determined, gave

t.	Sp. rotation.	Mol. rotation.
13·6°	1·0591	6·208

This result is a little higher than that formerly given (6·121), but the specimen previously examined, although having a slightly lower specific rotation (13·2° 1·0571), had a higher density (*d* 15°/15° = 0·67037), which would cause this.*

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* It was stated at the time that this density was higher than that usually given, and was supposed to be owing to the greater purity of the product; as, however, the boiling point, expansion, and specific rotation were nearly identical with those of the new specimen examined, it seems probable that some slight error

Hexylene. Methylpropylethylene, $CH_3{\cdot}CH_2CH_2{\cdot}CH{:}CH{\cdot}CH_3$.

This substance, when first fractionated, left a small quantity of what appeared to be a polymerized product; but, on raising the temperature, it exploded violently, destroying the apparatus. The specimen examined boiled at 68—68·5°, corr. Hecht and Strauss (*Annalen*, 1874, 172, 62) give it as 67° at 737·9 mm. The density determination gave

d 4°/4°	0·6966.	*d* 15°/15°	0·6868.
d 10°/10°	0·6911.	*d* 20°/20°	0·6828.
d 25°/25°	0·6790.		

Hecht and Strauss found 0·6907 for 0°, whilst the above calculated for this temperature gives 0·7001.

The magnetic rotation, three times determined, gave

t.	Sp. rotation.	Mol. rotation.
15·6°	1·0991	7·473

Octylene. Hexylethylene, $CH_3{\cdot}[CH_2]_5{\cdot}CH{:}CH_2$.

The boiling point of the product examined was 122—123·5°, corr. The density determinations gave

d 4°/4°	0·7321.	*d* 15°/15°	0·7230.
d 10°/10°	0·7268.	*d* 20°/20°	0·7197.
d 25°/25°	0·7167.		

The magnetic rotation, twice determined, gave

t.	Sp. rotation.	Mol. rotation.
14·8°	1·0967	9·435.

Diamylene. Decylene. $C_{10}H_{20}$.

Constitution not established.

This was prepared by polymerizing amylene and fractioning the product; it boiled at 154·5—155·5°. The density determinations gave

d 4°/4°	0·7813.	*d* 15°/15°	0·7734.
d 10°/10°	0·7767.	*d* 20°/20°	0·7702.
d 25°/25°	0·7676.		

The magnetic rotation, twice determined, gave

t.	Sp. rotation.	Mol. rotation.
15·7°	1·1396	11·468.*

---

had been made in the density determination. If the old results be calculated with the new density the molecular rotation obtained is 6·194, a number very close to that given above.

* Otto Schonrock has measured the foregoing olefines, and for the first three,

Diallyl, $CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CH_2$.

For the specimen used in the following measurements, I am indebted to Mr. Lionel Jones. After being kept over sodium for some time, it boiled constantly at 59·1°, corr. The density determinations gave

d 4°/4° 0·7052. *d* 15°/15° 0·6952.
d 10°/10° 0·6995. *d* 20°/20° 0 6910.
d 25°/25° 0·6868.

The magnetic rotation gave

t.	Sp. rotation.	Mol. rotation.
14·5°	1·2857	8·420.

Dipropargyl, $CH{:}C{\cdot}CH_2{\cdot}CH_2{\cdot}C{:}CH$.

Mr. Lionel Jones also furnished me with this product, prepared from the diallyl tetrabromide. Its boiling point was 85·4°. As this product changes rather quickly on keeping, it was rectified, under 100 mm. pressure, immediately before the determination of its rotation and density. The density determinations gave

d 4°/4° 0·8032. *d* 15°/15° 0·7930.
d 10°/10° 0·7973. *d* 20°/20° 0·7888.
d 25°/25° 0·7849.

The magnetic rotation, once determined, gave

t.	Sp. rotation.	Mol. rotation.
14·8°	1·9100	10·435.

Isoprene, $CH_3{\cdot}CH{:}CH{\cdot}CH{:}CH_2$?

I am indebted to Professor Tilden for two specimens of this hydrocarbon, one prepared from American turpentine and the other from india-rubber. Both were carefully distilled just before examination.

1. Isoprene from turpentine. Boiling point, 36°, corr. Density

d 4°/4° 0·6874. *d* 10°/10° 0·6813. *d* 15°/15° 0·6768.
d 20°/20° 0·6730. *d* 25°/25° 0·6696.

The magnetic rotation, twice determined, gave

t.	Sp. rotation.	Mol. rotation.
17 6°	1·3606	7·615.

2. Isoprene from india-rubber. Boiling point, 36—37°, corr. Density

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obtained numbers which are only slightly lower than those given in this paper. His results for diamylene, however, do not accord well with the above (*Zeit. Physikal. Chem.*, 1893, 11, 757—758).

d 4°/4° 0·6856. *d* 10°/10° 0·6796. *d* 15°/15° 0·6748.
d 20°/20° 0·6705. *d* 25°/25° 0·6663.

The magnetic rotation, once determined, gave

t.	Sp. rotation.	Mol. rotation.
19°	1·3227	7·443.

It will be seen from the above that the two specimens do not give exactly the same results, the first having a slightly higher density and rotation than the second. The expansions by heat also are not quite identical, that of the first being the smallest.

	I.	II.
d 4°/4°	0·6874	0·6856
d 25°/25°	0·6696	0·6663
Diff. for 21°	0·0178	0·0193.

An endeavour to determine which of these two samples was the purer was made by titrating them with a solution of bromine in glacial acetic acid, isoprene forming a tetrabromide as shown by Tilden (*Chem. News*, 1882, **46**, 120), but the results were not satisfactory, the reaction is not quite definite, a little hydrogen bromide being formed, and probably some polymerization of the hydrocarbon taking place at the same time. The numbers obtained were—

Isoprene from turpentine. Mean of three determinations	68 parts absorbed 279·5 of bromine.
Isoprene from india-rubber. Mean of two determinations	68 parts absorbed 266·9 of bromine.

If the pure tetrabromide alone had been formed, 320 would have been taken up.

The results show that the isoprene from turpentine unites with a somewhat greater amount of bromine than that prepared from india-rubber. From this observation, however, little can be gathered, except that it shows that the two specimens were not equally pure; at the same time, the fact that the isoprene from turpentine combined with a larger amount of bromine, does not necessarily show that it was the purest, because it might contain an impurity absorbing a larger amount of bromine than isoprene itself.

Under these circumstances it will perhaps be best to take the average of the results obtained with both specimens, namely 7·529, as the rotation of this hydrocarbon; this is not likely to be far from the correct number.

On considering the foregoing results, it is seen that the olefines have very low densities, that of trimethylethylene at 15° being 0·6620, and that of diamylene 0·7734; but, notwithstanding this, their magnetic rotations are considerably higher than those of the corresponding paraffins. It is remarkable also that the boiling points of the first three given above, correspond very nearly with those of the corresponding normal paraffins, although they are not analogous in constitution, the boiling point of diamylene likewise does not differ much from that of diamyl.

Pentane	36·2°
Trimethylethylene	36·0
Hexane	69·0
β-Hexylene	68·2
Octane	125·5
Octylene	122·7
Diamyl	159·5
Diamylene	155·0

With respect to the molecular magnetic rotations of the olefines, these, when compared amongst themselves, do not give any regular differences for variation in composition by CH_2, because they are not similarly constituted, and therefore are not homologous. The following show what the differences are—

	Mol. rotation.	Diff. for CH_2.
Trimethylethylene	6·208	1·265
β-Hexylene	7·473	1·959 ÷ 2 = 0·979
Octylene	9·432	2·036 ÷ 2 = 1·018
Diamylene	11·468	

Considering that the first olefine in this table is a tri-, the second a di-, the third a mono-, and the fourth (according to Butlerow) a hexa-methyl derivative, these numbers are almost more closely related than might have been expected, and rather tend to show that the presence of the methyl group in olefines, does not affect the rotation so largely as it does in the paraffins.

It is somewhat remarkable, that in the comparison of octylene with diamylene, considering the supposed constitution of the latter, that the difference for CH_2 comes out very much the same as in the case of the paraffins, which is 1·023. The difference between hexylene and octylene is only 0·044 less than the normal. That trimethylethylene should behave differently from the other olefines is not strange, because it does not contain a CH_2 group as all the others do. So far as can be judged from these comparisons there is no reason for doubting that the difference for CH_2 between olefines of similar constitution is the same, as it is in the paraffin series.

The relationship of the rotations of the olefines to those of the paraffins is of interest, as will be seen from the following table.

Substance.	Mol. rotation.	Diff. for $-H_2$.
Trimethylethylene ..	6·208	+0 578
Pentane	5 630	
Hexylene	7·473	+0·827
Hexane......... ...	6·646	
Octylene	9·432	+0·740
Octane	8·692	
Diamylene.........	11·472	+0 734
Decane (cal.)	10·738	

The first difference for unsaturation by H_2 is somewhat analogous to the differences found for vinyl compounds; thus, for vinylic bromide, or bromethylene, it amounts to only 0·369, and for methylvinylic bromide, or methylbromethylene, it is 0·410 (*Trans.*, 1884, **45**, 568). The reason why trimethylethylene should behave differently from the other olefines has already been referred to. In reference to the other differences, they are smaller than are usually found in other series, the vinyl excepted, allyl displacements are the next lowest, being about 0·918, as in allylacetic acid, but the average difference is about 1·112 (*Trans.*, 1892, **61**, 803).

It is seen from the foregoing comparisons that it would be useful to have the rotations of several normal olefines for comparison so that their relationships to the paraffins might be established more clearly than is possible from those given above; nevertheless they probably give a fair idea of the subject.

The special point of interest in connection with diallyl is that it is doubly unsaturated, or unsaturated to the second degree, the character of the unsaturated carbon groups being the same as in two ethylenes or two double linkings. In dipropargyl, the conditions are still more interesting, inasmuch as it contains two acetylene, or threefold linkings ($-C\equiv C-$) and is unsaturated to the fourth degree, and it is of importance to see whether these two acetylene combinations act on the molecular rotations in a manner peculiar to themselves, or in the same way as might be expected from four doubly linked carbon groups, such as would exist if this hydrocarbon had the constitution $CH_2:C:CH·CH:C:CH_2$ instead of $CH:C·CH_2·CH_2·C:CH$. In considering this, it will be necessary to compare the molecular rotations of the entire series of compounds, from hexane to dipropargyl, but before doing so it will also be interesting to compare the boiling points, densities, and specific rotations of these substances.

Boiling Points.

Substance.	B. P.	Diff.
Hexane	69·0°	−1·0° for $-H_2$
Hexylene..............	68·2	−11·8 "
Diallyl................	59·1	+25·9 for $-H_4$
Dipropargyl...........	85·0	

Densities.

Substance.	d 15°/15°.	Diff.
Hexane..............	0·6739	0·0129 for $-H_2$
Hexylene............	0·6868	0·0084 „
Diallyl..............	0·6952	0·0978 for $-H_4$
Dipropargyl....... ..	0·7930	

Specific Rotations.

Substance.	Sp. rotation.	Diff.
Hexane.........	11° 0·9451	0·1540 for $-H_2$
Hexylene	15·6° 1·0991	0·1866 „
Diallyl	14·5 1·2857	0·6243 for $-H_4$
Dipropargyl.....	14·8 1·9100	

On comparing the above it is seen that dipropargyl has a considerably higher boiling point, density, and specific rotation than diallyl, or either of the other two hydrocarbons. In the boiling points, the ethylene, or double linkings, and difference of composition cause a reduction, the second being much greater than the first, which is but slight; probably a third or fourth would reduce it much more, whereas the two acetylene, or triple linkings, and difference of composition raise the boiling point nearly 26°. In the densities, the first double linking and difference of composition causes a rather larger rise than the second, which is but small, and therefore possibly a third or fourth would have a still smaller influence; the acetylene linkings, however, act in the opposite manner, dipropargyl having a much higher density than any of the other hydrocarbons under consideration. The *specific* magnetic rotations give variations of much the same order as the densities, so that all those physical properties, taken by *themselves*, show that the acetylene linkings evidently influence the properties of compounds in a manner different from the double linkings.

When, however, the molecular rotations are considered, in which not only the specific rotations but also the *densities* are used in the calculations, the results are found to be of a different kind, thus—

Substance.	Mol. rotation.	Diff.
Hexane..............	6·646	0·827 for $-H_2$
Hexylene	7·473	0·947 „
Diallyl	8·420	2·015 for $-H_4$
Dipropargyl..........	10·435	

These numbers when plotted out are found to be practically included in a regular curve, as will be seen in Plate 1, where the abscissæ refer to the degree of unsaturation and the ordinates the molecular rotations, showing that the rotations gradually increase

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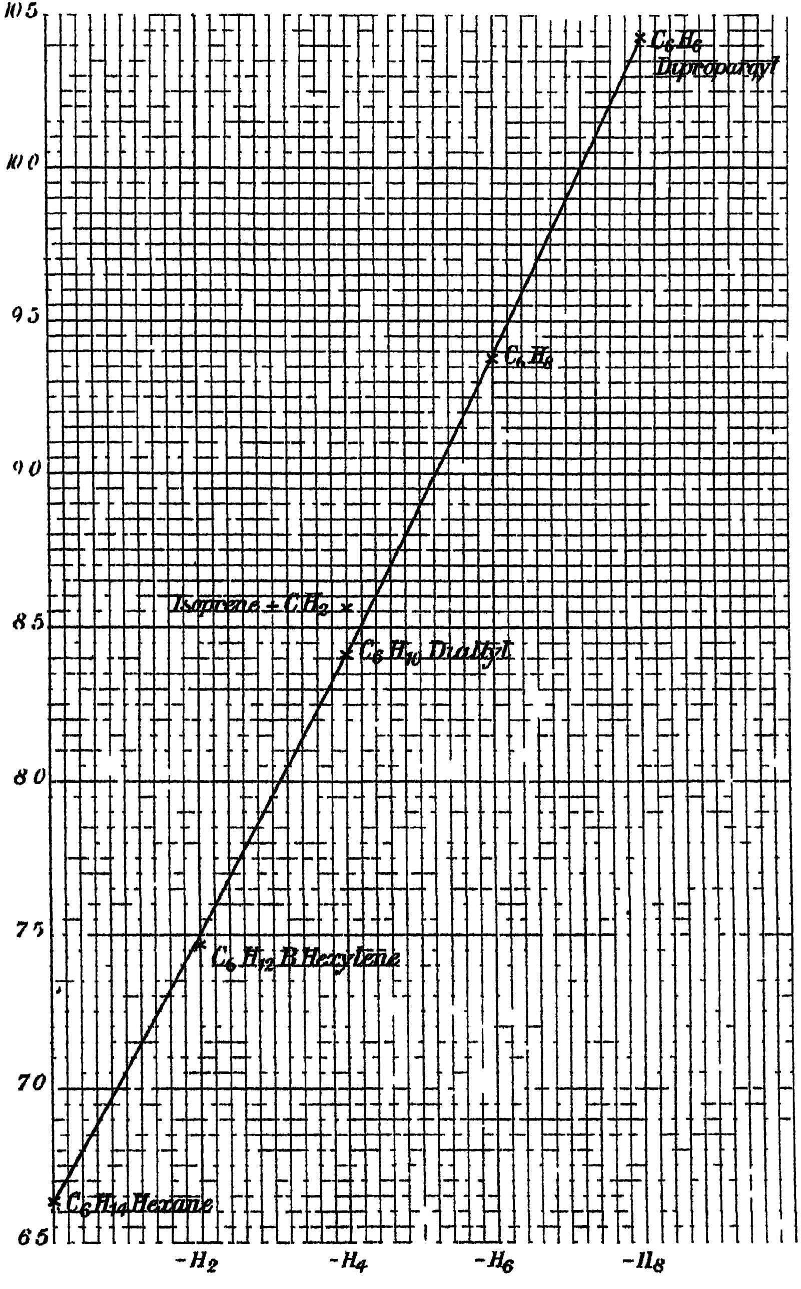
Fig 1.



with the unsaturation, no sudden change occurring between diallyl and dipropargyl. This curve also gives a value for the missing hydrocarbon, C_6H_8; if this be introduced, the progression of the numbers will be as follows.

Substance.	Mol. rotation.	Diff. for $-H_2$.
Hexane	6·646	
		0·827
Hexylene	7·473	
		0·947
Diallyl...............	8·420	
		0·980
C_6H_8............	9·400	
		1·035
Dipropargyl......	10·435	

So that the two acetylene or triple linkings in propargyl affect its molecular rotation in the same manner as would be expected if there were four ethylene or double linkings.

In the above comparisons, there is one inconsistency, inasmuch as the rotation of the hexylene is that of the β-compound and not that of the normal; this makes it of interest to examine the latter, although probably its rotation would not be very different from that of its isomeride.

As these results show that the effect of unsaturation on the rotations of these hydrocarbons progresses slightly with its extent, the first difference being 0·827 and the last 1·035, it may appear that this is inconsistent with some of the results previously published, in which the opposite was shown to occur (Trans., 1884, **45**, 561—562, and 1886, **49**, 212), but in these cases which refer to the ethylic allylmalonates and allylacetic acid, two unsaturated groups are associated with a single carbon atom, so that the results are not comparable.

It is of interest to notice that the rotation of dipropargyl is considerably lower than that of its ring isomeride, benzene, which is 11·280, showing a difference of no less than 0·845. This interesting point will be referred to in a future communication.

The only other hydrocarbon to be considered is *isoprene*, this only differs in composition from diallyl by CH_2; if, therefore, the value of this be added to its rotation, a comparison can be made.

Mol. rotation of isoprene from turpentine $+CH_2$ .... 7·615 + 1·023 = 8·638
Mol. rotation of isoprene from india-rubber .... 7·443 + 1·023 = 8·466
Mean...... 8·552

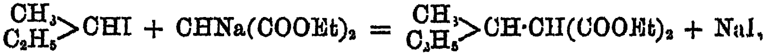
The rotation of diallyl is 8·420, and it will be observed that the product from india-rubber is the nearest to this; as isoprene is, however, not believed to be a true isomeride of diallyl, it probably would not give a rotation differing from that of the latter by exactly the value of CH_2. It will be better, therefore, to keep to the average value of the two products for the present, as previously proposed; this will make the rotation relatively a trifle higher than that of diallyl. The position of the rotation of this hydrocarbon, plus the value of CH_2, in reference to the curve formed by the C_6 compounds, is given on the Plate (p. 262). The foregoing comparisons go to show that the rotation found for isoprene is probably near the truth, and is consistent with that of a hydrocarbon unsaturated to the second degree.

XXXIII.—ββ-*Methylethylpropionic acid*,

$$\begin{matrix}CH_3\\C_2H_5\end{matrix}\!>CH\cdot CH_2\cdot COOH.$$

By W. H. BENTLEY, B.Sc.

DURING the course of experiments which are being carried on in the laboratories here, on the action of fused potash and soda on camphoric acid, various fatty acids have been obtained, and in order to determine their constitution, it was necessary to synthesise certain fatty acids hitherto unknown. At the suggestion of Dr. Perkin, I undertook the synthesis of ββ-methylethylpropionic acid, and to study its properties. Methyl ethyl ketone was chosen as the starting point, and this was first reduced to methylethylcarbinol by the action of sodium on its moist ethereal solution, and the alcohol then converted into secondary butylic iodide, $CH_3\cdot CHI\cdot C_2H_5$, by the action of iodine and phosphorus. This iodide, when treated with ethylic sodiomalonate, is readily converted into ethylic secondary butylmalonate,



$$\begin{matrix}CH_3\\C_2H_5\end{matrix}\!>CHI + CHNa(COOEt)_2 = \begin{matrix}CH_3\\C_2H_5\end{matrix}\!>CH\cdot CH(COOEt)_2 + NaI,$$

which, on hydrolysis and subsequent distillation, yields ββ-methylethylpropionic acid, thus—

$$\begin{matrix}CH_3\\C_2H_5\end{matrix}\!>CH\cdot CH\!<\!\begin{matrix}COOH\\COOH\end{matrix} = \begin{matrix}CH_3\\C_2H_5\end{matrix}\!>CH\cdot CH_2\cdot COOH + CO_2.$$

From the pure acid, which boils constantly at 196°, the following derivatives were prepared.

Ethylic salt, $C_5H_{11}\cdot COOC_2H_5$	b. p. 157—158°.
Amide, $C_5H_{11}\cdot CO\cdot NH_2$	m. p. 125°.
Anilide, $C_5H_{11}\cdot CO\cdot NH\cdot C_6H_5$	„ 88°.
Paratoluidide, $C_5H_{11}\cdot CO\cdot NH\cdot C_7H_7$	„ 75°.

Methyl ethyl ketone, $CH_3\cdot CO\cdot C_2H_5$.—This was prepared by Böcking's method (*Annalen*, 1880, **204**, 17), by the hydrolysis of ethylic methylacetoacetate, by boiling it with one-fourth its weight of dilute sulphuric acid (20 per cent.) for six hours in a flask provided with a reflux condenser. The whole was then distilled in a current of steam, the distillate mixed with potassium carbonate, extracted several times with ether, and the ethereal solution washed successively with small quantities of water to remove alcohol; it was then dried with calcium chloride, and the fraction boiling at 80—82° collected.

Secondary Butyl Alcohol; Methylethylcarbinol, $CH_3\cdot CH(OH)\cdot C_2H_5$.—The action of sodium amalgam on aqueous solution of the ketone gave such a small yield of methylethylcarbinol that this method was abandoned in favour of the following. The ketone was dissolved in five times its volume of ether, poured on to a strong solution of caustic soda contained in a bottle fitted with a reflux condenser, and small pieces of sodium were then dropped into the mixture; the white substance, which separated during the reduction, probably the sodium compound of the alcohol, was decomposed by the addition, from time to time, of small quantities of water, and the whole was kept cool by immersing the bottle in water. When about twice the theoretical quantity of sodium had been added, the ethereal solution was separated from the caustic soda, dried with potassium carbonate, and fractionated. The unreduced ketone was put back again into the bottle and treated with more sodium, whilst the fraction 96—110°, consisting chiefly of the alcohol, was carefully fractioned, the portion boiling at 98—103° being employed in the subsequent experiments; the boiling point of methylethylcarbinol, according to Lieben (*Annalen*, 1869, **150**, 114), is 99° (738·8 mm.).

Secondary Butylic Bromide, $CH_3\cdot CHBr\cdot C_2H_5$.—This substance, which does not seem to have been previously examined, was prepared by heating the alcohol with three times its volume of fuming hydrobromic acid for one hour in a reflux apparatus, a stream of hydrogen bromide being passed through the liquid during the operation. On adding water to the product, the bromide separated as a heavy oil. After drying over calcium chloride and fractionating, it boiled constantly at 89—90° and gave the following numbers on analysis.

Found .... Br = 58·62

Theory for C_4H_9Br .... 58·39.

Secondary Butylic Iodide, $CH_3\cdot CHI\cdot C_2H_5$, has been obtained from erythrol (De Luynes, *Bull. Soc. Chim.*, **2**, 3), from ethyldichlorether, $C_2H_3Cl(C_2H_5)O\cdot C_2H_5$ (Lieben, *Annalen*, **150**, 96), and from normal butylene (Würtz, *Annalen*, 1869, **152**, 23), in each case by the action of hydriodic acid. As the result of several experiments, I found that the simplest way of preparing it was by treating secondary butyl alcohol with iodine and phosphorus in the usual way. To the mixture of the alcohol (65 grams) with red phosphorus (10 grams), iodine (111 grams) was added in small quantities at a time. After standing for some time, the whole was heated in a reflux apparatus, distilled, and the distillate washed successively with a dilute solution of sodium hydrogen sulphite, and with water; it was then dried with calcium chloride and fractionated. The pure iodide is a colourless liquid boiling at 118°, the yield was almost quantitative.

Ethylic Secondary Butylmalonate, $(CH_3)(C_2H_5)CH{\cdot}CH(COOEt)_2$.—In the first experiments made with the object of obtaining this compound, the bromide was employed; sodium (9 grams) was dissolved in alcohol, ethylic malonate (62 grams) added, and the mixture digested with secondary butylic bromide (53 grams), until the reaction was neutral. On adding water, extracting with ether, and distilling the washed and dried ethereal solution, the oily residue left when the ether had passed over distilled between 195° and 198°, and on examination was found to consist entirely of ethylic malonate. The bromide had evidently been decomposed into an unsaturated hydrocarbon and hydrogen bromide; and the latter, acting on the ethylic sodiomalonate, gave sodium bromide and ethylic malonate; this behaviour appears to be by no means uncommon, several other instances of a similar character having been observed here.

Subsequent experiments showed that secondary butylic iodide behaves in this respect quite differently from the bromide, as when digested in alcoholic solution with ethylic sodiomalonate, a very good yield of ethylic secondary butylmalonate is obtained.

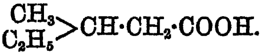
Sodium (16 grams) was dissolved in ethylic alcohol (170 grams), ethylic malonate (109 grams) added, and the whole digested with secondary butylic iodide (125 grams) for two hours. The neutral product was cooled, diluted with 3 vols. of water, extracted with ether, and the ethereal solution distilled after being washed with water and dried with calcium chloride; the residue left, after the ether had passed over, was twice fractioned. The pure ethylic secondary butylmalonate thus obtained boiled at 228—231°, and, on analysis, gave the following results.

Found .... $C = 60{\cdot}54$; $H = 9{\cdot}21$ per cent.
Theory for $C_{11}H_{20}O_4$ $C = 61{\cdot}11$; $H = 9{\cdot}26$ „

Secondary Butylmalonic acid,

$\begin{matrix}CH_3\\C_2H_5\end{matrix}{>}CH{\cdot}CH(COOH)_2$.—In order to prepare this acid, the purified ethereal salt was boiled with an excess of alcoholic potash for two hours, the product diluted with water, and evaporated until all the alcohol had been removed. The solution was then acidified and extracted with ether, and the ethereal solution, after drying over calcium chloride and evaporating, deposited a thick, oily acid; this, on standing, commenced to crystallise. The crude acid, which undoubtedly consisted of secondary butylmalonic acid, was not analysed, however, but directly converted into $\beta\beta$-methylethylpropionic acid.

$\beta\beta$-Methylethylpropionic acid,



$$\begin{matrix}CH_3\\C_2H_5\end{matrix}\!\!>CH\cdot CH_2\cdot COOH.$$

This acid is formed quantitatively by heating secondary butylmalonic acid in a retort until the evolution of carbon dioxide ceases, and then distilling the residue. It is an unpleasant smelling liquid, which boils at 196° under a pressure of 764 mm., and possesses properties very similar to those of caproic acid.

0·1500 gave 0·3416 CO_2 and 0·1438 H_2O. C = 62·11; H = 10·65.
$C_6H_{12}O_2$ requires C = 62·07; H = 10·35 per cent.

The following derivatives of this acid have been prepared and examined.

Ethylic Salt, $CH(CH_3)(C_2H_5)\cdot CH_2\cdot COOC_2H_5$.—This was prepared by passing dry hydrogen chloride into a cooled solution of the acid in ethylic alcohol; when the liquid was thoroughly saturated with the gas, it was allowed to stand for a considerable length of time, and then again saturated. After 24 hours, the product was poured into water, the ethylic salt extracted with ether, &c., in the usual way, and the oily residue purified by fractionation.

Ethylic $\beta\beta$-methylethylpropionate is a colourless liquid, which boils constantly at 157—158°, and has an odour resembling that of the ethereal salts of the higher fatty acids. On analysis, the following result was obtained.

Found	C = 66·68; H = 11·36 per cent.	
Theory for $C_8H_{16}O_2$.	C = 66·66; H = 11·11	,,

The Amide, $CH(CH_3)(C_2H_5)\cdot CH_2\cdot CONH_2$.—The ethylic salt, with three times its volume of concentrated ammonia solution, was heated at 170—180° for 10 hours in a sealed tube. When cold, the contents of the tube were still liquid, but, on shaking, needle-shaped crystals separated; these were collected by aid of the pump, washed with concentrated ammonia, and dried on a porous plate. The mother liquor, on extraction with ether, yielded a considerable quantity of the amide, but the extraction had to be repeated at least 10 times on account of the great solubility of the amide in the aqueous liquid. The ethereal solution, after being dried with calcium chloride, was evaporated to a small bulk on the water bath, poured into a basin and put aside to crystallise. The amide, after drying on a porous plate, was analysed.

Found................ $N = 11{\cdot}86$ per cent.
Theory for $C_5H_{11}{\cdot}CONH_2$ $N = 12{\cdot}17$ „

The amide melts at 125° and crystallises from water, ether, or benzene in plates. It is readily soluble in warm water, benzene, and alcohol, sparingly so in pure ether or light petroleum.

The *anilide*, $CH(CH_3)(C_2H_5){\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}C_6H_5$, was prepared by boiling a mixture of the acid with aniline for 20 hours in a flask fitted with a reflux tube. When cold, the contents of the flask were dissolved in ether, the solution washed with hydrochloric acid to remove aniline, then with water, dried with calcium chloride, and evaporated. The dark-coloured, solid residue, after purification by repeated recrystallisations from light petroleum with the aid of animal charcoal, yielded a colourless, crystalline product, which melted at 88°, and gave the following results on analysis.

Found.. .. .. $N = 7{\cdot}3$ per cent.
Theory for $C_5H_{11}{\cdot}CO{\cdot}NH{\cdot}C_6H_5$ $N = 7{\cdot}32$ „

This anilide is very readily soluble in benzene and alcohol, but only sparingly in water or cold light petroleum. When heated in small quantities, it distils without decomposition.

The *paratoluidide*, $CH(CH_3)(C_2H_5){\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}C_7H_7$, was prepared and purified in precisely the same manner as the anilide, with the exception that the mixture of the acid with the paratoluidine was heated for a shorter time (about 15 hours) on account of the higher boiling point of toluidine. Analysis.

Found........................ ... $N = 6{\cdot}97$ per cent.
Theory for $C_5H_{11}{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}CH_3$... $N = 6{\cdot}83$ „

This toluidide crystallises from light petroleum in needles, and melts at 75°: in its general properties it closely resembles the corresponding anilide.

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XXXIV.—*Volumetric Estimation of Manganese.*

By JOSEPH REDDROP and HUGH RAMAGE.

Methods previously employed.

THE number and nature of the processes for determining manganese in ores, irons, steel, and alloys proposed during recent years show the importance of a rapid and accurate method for the determination of this element.

The gravimetric process, so generally described in books, takes several hours, and requires almost constant attention; further, the results given by it are liable to be interfered with by the presence of nickel, copper, and certain other elements, which are co-precipitated with and generally weighed with the manganese oxide. When these foreign substances are previously removed, and the manganese weighed as pyrophosphate, there may be considerable error, unless a correction is made for the solubility of the ammonium manganous phosphate; moreover, the analysis is very long and tedious.

Pattinson's volumetric method is more accurate and much shorter than the gravimetric method, but appears to have given different results in different chemists' hands. We have found it an accurate and in most respects a satisfactory process, but it is not well adapted for determining small quantities; considerable time is required to wash the precipitate in the case of large quantities, and the titration with potassium dichromate is somewhat tedious; moreover, the fumes from the bleaching powder or bromine water employed are decidedly objectionable. Further, nickel, cobalt, copper, and, to a much greater extent, chromium, interfere and cause inaccuracies (*Jour. Soc. Chem. Ind.*, 1891, 333).

The lead peroxide colorimetric process is very useful and accurate for determining quantities of manganese up to about 2 per cent., as in steel and iron directly, and also in alloys after the separation of the other metals.

Proposed Method.

As one of us had for a long time sought for a rapid and accurate method of analysis applicable to steels and ferromanganese, and had experimented with the different processes proposed, although without discovering anything satisfactory, a method proposed by L. Schneider (*Dingl. Polyt. J.*, **269**, 224) promised so well that a study of it was made jointly by us in 1890. After introducing some modifications, which, as will be seen from our experiments, add to the accuracy of the process, we can now, after four years' use, recommend it as a thoroughly trustworthy method for the determination of manganese. It is much shorter even than Pattinson's process, as, after the dissolution of the sample is effected, the result may be obtained in less than 15 minutes.

Schneider's method depends primarily on the fact that in presence of a large quantity of nitric acid a manganous salt is rapidly and completely oxidised to permanganic acid by bismuth tetroxide at the ordinary temperature. The solution is then filtered through an asbestos filter, and the permanganic acid titrated with a standard solution of hydrogen peroxide.

The method is very simple in principle, but we soon discovered that, unless modified, serious errors might be introduced; with the modifications we propose, however, the quantity of manganese can be determined to within 0 05 milligram.

Reagents used in the Analysis.

The necessary reagents are—

Standard N/10 potassium permanganate.
5E* nitric acid.
Hydrogen peroxide, approximately N/10.
Sodium bismuthate.

Standard N/10 *Potassium Permanganate.*—It is stated by some chemists that this reagent decomposes too rapidly for regular use, but we have found that if prepared from the pure salt this is not the case. A solution made in March of last year was carefully titrated six months later, when the 2-litre bottle was nearly empty, and the error was 0·15 c.c. per 100 c.c. The salt and the water employed must be absolutely free from chlorine. The solution is made by dissolving 3·16 grams of the pure salt in water, and diluting to 1 litre; as thus made, it is quite accurate. When not in use it should be kept in the dark.

Preparation of 5E Nitric acid.—Take 310 c.c. of pure, colourless nitric acid of sp. gr. 1·42, dilute to 1 litre, and allow it to stand exposed to the air for at least 24 hours, so that the nitrous acid may be oxidised.

Hydrogen Peroxide, approximately N/10.—Hydrogen peroxide in aqueous solution decomposes on keeping, but we find by experiments (given below) that when dissolved in nitric acid of about normal strength it remains almost constant, there being no appreciable change in a week, even when quantities of from 50 to 100 c.c. are titrated.

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* The symbol "E" used in this paper is a contraction of the word "equivalent" and is employed to denote the number of milligram equivalents of reacting substance contained in 1 c.c. of reagent. Thus, E nitric acid contains 63 milligrams HNO_3 per c.c., 4E nitric acid 4 times this quantity, 16E acid 16 times this quantity, and so on. 16E nitric acid has the sp. gr. 1·4268 at 15·5° C., but the acid sold as sp. gr. 1·42 is employed in all cases as being sufficiently near to the true sp. gr. for our purpose. The dilute acids are made by simply diluting 16E acid with water to the requisite degree. It will thus be seen that E reagents are made on the same principle as the N reagents in volumetric analysis, the only difference being in the *degree of accuracy* with which they are made and measured out for use. See *Chem. News*, 1890, 61, 245.

	Titrated. 10/5/90.	Titrated. 18/6/90.	Titrated. 26/7/90.
10 c.c. of $KMnO_4$ required of hydrogen peroxide, diluted with water........	9·8 c.c.	10·9 c.c.	12·1 c.c.
10 c.c. of $KMnO_4$ required of hydrogen peroxide, in E/10 nitric acid	9·9 „	10·0 „	10·25 „
10 c.c. of $KMnO_4$ required of hydrogen peroxide, in E nitric acid	9·9 „	9·9 „	10·0 „

All the samples of hydrogen peroxide which we have obtained commercially have been contaminated with chlorides, and this probably accounts, to some extent at least; for the slow decomposition which takes place in the above nitric acid solution. The presence of chlorides in the hydrogen peroxide is very objectionable, and if it amounts to more than traces it interferes with the accuracy of the results.

We therefore prefer to prepare the hydrogen peroxide absolutely free from chlorine in the following manner.

Take 3·9 grams of sodium peroxide free from chlorides, and add to 500 c.c. of water, then add 220 c.c. of 5E nitric acid, and dilute to about 800 c.c.; the solution will be found to be somewhat too strong. It may then be titrated with standard N/10 permanganate, and adjusted to exactly N/10 hydrogen peroxide if desired.

Sodium Bismuthate—Schneider uses bismuth peroxide prepared by Fremy's method, as follows:—Equal parts of bismuth oxide and potassium chlorate are first heated together, and then fused with two parts of caustic soda. The fused mass is lixiviated with water, and the insoluble powder, containing soda and bismuthic acid, is finally treated with water containing 5 per cent. of nitric acid, washed, and dried at 100°. As this powder retains some chlorine compounds which interfere with the accuracy of the analysis, we do not recommend this method of preparation. We employ the sodium bismuthate prepared *without the use of any chlorine compound.* The preparation of this salt with a maximum oxidising power has given us considerable trouble, but we have succeeded at last by heating 20 parts of caustic soda nearly to redness in an iron crucible, and adding in small quantities at a time 10 parts of basic bismuth nitrate, previously dried in a water oven. Two parts of sodium peroxide are then added, and the brownish-yellow fused mass is poured out on an iron plate to cool; when cold, it is broken up in a mortar, extracted with water, and collected on an asbestos filter. The residue, after being washed four or five times by decantation, is dried in the water oven, then broken up, and passed through a fine sieve. We hope to communicate a detailed account of our work on the preparation in a second paper. Our crucibles were made of Farnley iron, as this contains only a trace of manganese; this does not now seem to be of any importance, however, as any manganese present in the materials employed is converted into sodium permanganate by the fusion with excess of sodium peroxide, and is afterwards dissolved and removed by the water, thus leaving the sodium bismuthate free from manganese.

Oxidising Power of the Sodium Bismuthate.—This may be determined by adding 20 c.c. of the hydrogen peroxide solution to about 0·25 gram of the sample, and, when dissolved, titrating the excess of hydrogen peroxide with N/10 potassium permanganate. One gram of our preparation has an oxidising power equal to 60 c.c. of N/10 reagent. Different batches of the preparation vary slightly in strength.

The Asbestos Filter.—This may be made in the tube form generally used, but we prefer the Gooch cone, as described in *Chem. News*, 1878, **37**, 181, and in Blair's *Analysis of Iron*, p. 26, Fig. 20. It may be prepared and washed in about a minute, and may be used several times before it becomes blocked. The asbestos is prepared by triturating the fibres in a mortar with strong hydrochloric acid, and, after transferring to a beaker, heating on a water bath for half an hour. The portion that remains longest in suspension when the deposit is stirred up with water makes the closest filter, but as the residual bismuth peroxide is comparatively coarse, a satisfactory and more rapid filter may be made by selecting the coarser asbestos for this purpose. This must be washed thoroughly free from hydrochloric acid.

Notes on the Method.

Schneider after oxidising the manganese in a 5E nitric acid solution, filters and titrates with hydrogen peroxide, but we found that the permanganic acid decomposed even in an E nitric acid solution, and that the rate of decomposition increased with the strength of the acid as shown in Table I.

TABLE I.—*Experiments to Determine the Rate of Decomposition of N/10 Permanganate in Nitric acid of from E to 5E Strength, on Standing Three Hours, 20 c.c. of Solution being used in each case.*

Strength of nitric acid.	Decomposition of permanganate per cent.
E	3·5
2E	4·0
3E	4·25
4E	5·5
5E	6·5

We then made experiments to ascertain the rate of the decomposition, under the conditions realised in the analysis. The filtrate containing the permanganic acid resulting from the treatment of 0·11 gram of ferromanganese containing about 80 per cent. of manganese was diluted to 250 c.c. and portions were titrated as follows.

TABLE II.

Volume.	Time allowed for decomposition.	Volume of H_2O_2 required.
50 c.c.	0 hr. 12 mins.	15·45 c.c.
50 „	0 „ 42 „	15·35 „
50 „	1 „ 12 „	15·25 „
50 „	3 „ 12 „	15·10 „
45 „	5 „ 42 „	13·2 = 14·7 for 50 c.c.

These experiments show that all the results obtained by Schneider's method will be below the truth, and further, that as the time occupied in filtering varies, the error will also vary. We therefore modified the process by allowing the filtrate to drop directly into a measured quantity of hydrogen peroxide, which, as we have shown above, undergoes no appreciable decomposition in a nitric acid solution. The results obtained by the modified process are, in the analysis of ferromanganese, 0·6 to 0·7 per cent. higher than by Schneider's method. This large difference is partially due to the agitation produced by the filtrate falling in drops from the filter.

We find the best strength of nitric acid in which to oxidise the manganese is between 3E and 5E; we adopt 4E. In other words, our solution contains one-quarter its volume of nitric acid, sp. gr. 1·42.

Hydrogen peroxide and permanganic acid may be titrated in any strength of nitric acid between 5E and E/5 without error.

Lead peroxide oxidises only about one-third of the manganese present in an 80 per cent. alloy, when substituted for the bismuth compound.

Nitric acid of sp. gr. 1·42 sometimes contains oxides of nitrogen in considerable quantity, but if mixed with three times its volume of water, and allowed to stand for 24 hours, not more than a mere trace remains insufficient to interfere with the working of this process.

The solution, after the analysis, is generally colourless, showing that the combined carbon has been completely oxidised.

PARTICULARS OF THE ANALYSIS.

I. *Ferromanganese* (containing over 20 per cent. manganese).

Dissolution of sample.—Weigh out 0·55 gram, place in a flask of about 200 c.c. capacity, add 15 c.c. of dilute nitric acid (5E) and boil until the sample is decomposed, then add 15 c.c. of nitric acid sp. gr. 1·42, and boil until the carbonaceous matter dissolves, cool, transfer to a 250 c.c. measuring flask, dilute to the mark, and mix.

Oxidation and Titration.—Measure out 20 c.c. of nitric acid, 1·42, 15 c.c. of water, and *exactly* 50 c.c. of the ferromanganese solution. Cool to about 16° C., add 4 grams of sodium bismuthate, stir for three minutes, and allow the residue to settle for two minutes. Filter through an asbestos filter, connected with a filter pump, into a flask containing 90 c.c. of the hydrogen peroxide reagent, and wash the residue with dilute nitric acid until the washings are colourless. Titrate the excess of hydrogen peroxide with N/10 potassium permanganate, stopping at the point where a drop colours the liquid for at least 30 seconds. Each c.c. of N/10 hydrogen peroxide reduced by the filtrate is equal to 1 per cent. of manganese in the sample.

Titration of the Hydrogen Peroxide.—The 90 c.c. of hydrogen peroxide used above may be conveniently measured with a 30 c.c. pipette, and its strength determined by titrating 60 c.c. (measured with the same pipette) with N/10 potassium permanganate after adding 25 c.c. of 5E nitric acid, free from nitrous acid.

II. *Spiegel and Silico-Spiegel* (containing up to 25 per cent. of manganese).

Dissolution of Spiegel.—Treat 0·55 gram as in the case of ferromanganese, with 15 c.c. of 5E nitric acid, but use only 10 c.c. of the stronger acid, and dilute the solution to 50 c.c.

Dissolution of Silico-Spiegel.—Boil 0·55 gram very finely powdered, in 20 c.c. of dilute sulphuric acid (5E); if only a very small residue remains, decant the clear solution and boil the residue with 6 c.c. of fresh acid until dissolved. If the sulphuric acid does not attack the sample readily, add some strong hydrochloric acid; when the sample is dissolved, add 1 c.c. of sulphuric acid of sp. gr. 1·84, and boil down to decompose all the chlorides and completely expel the hydrochloric acid, then add water and dilute to 50 c.c.

Oxidation and Titration.—The manganese is oxidised by adding 2 grams of sodium bismuthate to a liquid containing:

	Spiegel.	Silico-spiegel.
Of the above solution	10 c.c.	10 c.c.
Nitric acid, 1·42	8 „	10 „
Water	22 „	20 „

The nitric acid in each is 4E, and the sulphuric acid in the silico-spiegel E/2. The filtrate is run into 25 c.c. of hydrogen peroxide solution, and the excess of the latter titrated as in the ferro-manganese.

In the analysis of ferromanganese and spiegel, 0·11 gram of sample may be weighed out directly if preferred, but care must be taken to avoid the slightest loss.

III. *Wrought Iron, Steel, and Pig Iron* (containing less than 5 per cent. of manganese).

Dissolution of sample.—Weigh out 1·1 gram of the sample, and place it in a boiling tube $1\frac{1}{2}$ inches in diameter; add 30 c.c. of dilute nitric acid (5E), and boil. If a part remains undissolved, decant the solution, filtering off the carbonaceous matter if necessary, and add more dilute nitric acid up to 25 c.c. If the sample dissolves completely at once, use the 25 c.c. of acid to wash the tube and filter paper. If the sample contains much silicon, care must be taken when boiling not to concentrate the acid, or the silicic acid will separate in a form which completely blocks the filter.

Oxidation and Titration.—Cool to about 16°, oxidise with 2 grams of sodium bismuthate, and filter into an empty flask. The time of filtration should not exceed 15 minutes.* A slight excess of hydrogen peroxide is now added, and the excess titrated as in the preceding analysis.† Each c.c. of N/10 hydrogen peroxide reduced by the sample is equal to 0·1 per cent. of manganese.

Experiments made to test the accuracy of the method.

A quantity of ferromanganese was powdered, mixed, and used as a standard. Two determinations of the manganese in this sample by the ordinary gravimetric method gave 80·95 and 81·04 per cent. respectively. The precipitates however contained oxides of iron, copper, and nickel, corresponding to 0·37 per cent of manganese, but were free from silica. Deducting these impurities, we get 80·58 and 80·67 per cent. of manganese respectively, giving a mean result of 80·63 per cent. Three determinations of manganese by Pattinson's method gave 80·7 per cent. in each case.

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* The large quantity of ferric nitrate in the filtrate tends to the decomposition both of permanganic acid and hydrogen peroxide, the latter less than the former. Where a very accurate result is desired, the analysis should be completed without unnecessary delay.

† If the quantity of manganese appears less than 0·1 per cent., transfer the filtrate to a Nessler cylinder, and determine the manganese colorimetrically by adding N/10 permanganate to an equal volume of 5E nitric acid in another cylinder for comparison. By this method as small a quantity as 0 01 per cent. of manganese may be estimated.

The determinations made by the method under examination show that it gives results agreeing with the above, and also that within wide limits the result is not affected by the extent to which the solution is diluted during oxidation and titration.

Standard ferromanganese taken.	Volume of solution when oxidised.	Result. Mn. per cent.
0·11 gram.	20 c.c.	80·67
0·11 „	40 „	80·69
0·11 „	80 „	80·69
0·11 „	160 „	80·64

The strength of the nitric acid was 4E in each experiment, but in the first a quantity of acid equal to that neutralised by the sodium bismuthate was added in excess of that required to make the solution 4E.

A determination made by Schneider's original method gave 80·07 per cent., showing the error caused by the decomposition of the permanganic acid during filtration.

In an experiment made to test the effect of sulphuric acid, 0·11 gram of ferromanganese, oxidised in 80 c.c. of 4E nitric acid, and E sulphuric acid, gave 80·72 per cent. of manganese. When oxidised in 80 c.c. of 4E sulphuric acid, with no nitric acid, the result was only 73·1 per cent.

The following experiments show the accuracy of the method in determining small quantities of manganese.

To a solution of 1·1 gram of steel containing 0·075 per cent. of manganese, 6·465 per cent. of manganese was added, making the total quantity of manganese equal to 6·54 per cent. The quantity found was 6·48 per cent.

In a second experiment with steel, in which manganese equal to 1·00 per cent. was present, 0·99 per cent. was found.

In a third experiment with steel, in which 0·1 per cent. was present, 0·085 per cent. was found.

The following experiments were made to test the extent to which the metallic impurities, liable to be present in manganese alloys, interfere:—

		Per cent.
Standard ferromanganese	gave	80·69
,, ,, with chromium equal to 5 per cent. added	,,	80·97
,, ,, ,, copper equal to 5 per cent. added	,,	80·77
,, ,, ,, nickel equal to 5 per cent. added	,,	80·77
,, ,, ,, cobalt equal to 5 per cent. added	,,	80·97

We also observed that sodium bismuthate when added to a nitric acid solution of a salt of chromium, very slowly but completely oxidised the chromium to chromic acid.

In the analysis of ores, &c., of manganese, it will be necessary to make a 4E nitric acid solution of the sample free from chlorides, and containing not more than E sulphuric acid. The analysis may then be made in a manner similar to those already described.

In conclusion we desire to acknowledge our indebtedness to Mr. F. W. Webb, Superintendent of the L. and N.W. Railway Works at Crewe, for his kind permission to carry out the above experiments in the laboratory connected with the works.

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XXXV.—*The Sulphides and Polysulphides of Ammonium.*

By W. P. Bloxam, B.Sc. (Lond.), Royal Naval College, Greenwich.

I. *Oxidation Changes of Ammonium Hydrosulphide.*

It is a matter of common experience that the laboratory reagent known as ammonium hydrosulphide or ammonium sulphide is subject to change on contact with air. The solution prepared by saturating aqueous solution of ammonia with hydrogen sulphide is colourless at first, but, on exposure to air, it soon acquires a yellow colour, due to polysulphides; on adding an acid, this solution is decolorised, hydrogen sulphide being evolved, and sulphur deposited. On prolonged exposure to air, the yellow solution loses its colour and deposits sulphur.

My attention was first directed to the oxidation changes of ammonium hydrosulphide by the failure of a yellow solution to precipitate manganese sulphide on adding it to an aqueous solution of manganous sulphate; the solution was reserved for examination, but, on the following day, it was found to be colourless.

Two distinctly different views have been held as to what takes place during the oxidation. According to the one view, part of the ammonium hydrosulphide is decomposed by oxidation, yielding ammonia, water, and sulphur; of the latter, one portion acts on the remaining ammonium hydrosulphide to form ammonium bisulphide; another portion is oxidised, forming a thiosulphate, whilst the remainder is deposited. The other view assumes that ammonium hydrosulphide is directly oxidised with formation of ammonium bisulphide and thiosulphate in molecular proportion, sulphite and sulphate being formed when the solution becomes colourless.

The first point was to determine what ammonium compounds, other than sulphide and polysulphide, were present, and this involved the removal of sulphide and polysulphide, and the recognition in the filtrate of sulphite, thiosulphate, and sulphate. A scheme for separation is given by Fresenius ("Chemical Analysis—Qualitative, translated by C. E. Groves from the 15th German Edition," p. 194), but it was found to require modification before successful results could be obtained, owing to the difficulty of removing the last traces of hydrogen sulphide. An account of the modified method of analysis will appear in another journal. The experiments made showed that during the oxidation of ammonium hydrosulphide solutions traces of ammonium sulphite are always present, but that sulphate is not formed, ammonium thiosulphate being the end product.

These changes may be explained as follows:—In the first stage, polysulphide alone is formed, for after removal of sulphide and polysulphide by means of cadmium carbonate, the filtrate is free from oxidised sulphur compounds.

At the surface of the liquid some of the aqueous solution of ammonium hydrosulphide is resolved into ammonia, water, and hydrogen sulphide, the latter undergoing oxidation and yielding water and sulphur. This sulphur then acts on ammonium hydrosulphide, forming polysulphide and liberating hydrogen sulphide, the action continuing until the highest polysulphide mixture possible for the concentration is formed. This constitutes the first stage of the action, the maximum colour being developed, and the solution being free from oxidised sulphur. It is not possible to state with certainty whether one polysulphide or a mixture is obtained, but the results of experiments, to be described later, prove that, even when dilute solutions of ammonium hydrosulphide are acted on by sulphur, high polysulphides are formed from the first. There is not the slightest ground for supposing ammonium bisulphide to be formed.

In the second stage, the polysulphides are acted on by oxygen, sulphur being liberated.

$$(NH_4)_2S,S_x + O = 2NH_3 + H_2O + S.S_2.$$

In the third stage, the sulphur acts on ammonia as follows :—

$$4NH_3 + 4H_2O + S_3 = (NH_4)_2SO_3 + 2NH_4{\cdot}HS + H_2O,$$

resulting in the production of ammonium sulphite and hydrosulphide.

In the fourth stage, it will be observed that there are now two modes in which the sulphur may combine, namely, by union with ammonium sulphite, thereby transforming it into thiosulphate, or by acting on the ammonium hydrosulphide whereby more polysulphide is formed.

The absence of ammonium sulphate as an oxidation product is the more remarkable when the great affinity exhibited by ammonium sulphite for oxygen is considered. Experiments with the salt,* $2(NH_4)_2SO_3 + 3H_2O$, show that when moist it is rapidly transformed into sulphate in contact with air, much heat being evolved. On the other hand, the affinity of ammonium sulphite for sulphur is great, a solution of the salt dissolving sulphur with great rapidity, whilst, if crystals of the sulphite be added to a polysulphide solution, the latter is decolorised, the sulphite becoming thiosulphate at the expense of the polysulphide. Seeing that ammonic sulphite exhibits great affinity for both oxygen and sulphur, whilst as an experimental fact no sulphate is formed, it may be possible that the sulphite acquires the sulphur necessary to transform it into thiosulphate from polysulphides present in solution.

With a view to test the above explanation, experiments were made on the action of sulphur on ammonia solution. It was found that in an open vessel strong ammonia solution is not acted on by finely powdered sulphur, even if the solution be boiled. But if ammonia solution be heated with sulphur in a sealed tube in the water bath, action takes place; a solution of polysulphide, of colour intensity increasing with the strength of the ammonia, is obtained, and the solution contains ammonium thiosulphate, but no sulphate, and only traces of sulphite.

Analyses of the products of oxidation of solutions of ammonium hydrosulphide served to substantiate in general outline the theory of change put forward. At the same time, no means were to hand for determining the values of certain necessary factors, namely, the relative proportions of ammonia existing in the free state and as ammonium hydrosulphide, together with the exact nature of the polysulphide present. All that could be done was to determine the relations between total ammonia, sulphur present as sulphide and polysulphide, and the oxidised sulphur.

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* Being unable to obtain by purchase ammonium sulphite or ammonium thiosulphate in a state of purity, Mr. W. B. Giles kindly undertook their preparation, and was eminently successful. An account of the preparation and properties of these salts will appear in another journal.

It is to be noted that in previous accounts of changes occurring no share has been allotted to carbon dioxide in effecting the decomposition of ammonium hydrosulphide and polysulphide solutions. It is found that if pure washed carbon dioxide be passed into solutions of ammonium hydrosulphide, a steady evolution of hydrogen sulphide takes place, and crystals of ammonium hydrogen carbonate are deposited, but no polysulphide is formed. Polysulphides of ammonium are also readily decomposed on passing carbon dioxide through their solutions, hydrogen sulphide being evolved and sulphur deposited.

The paper published by Divers and Shimidzu (Trans., 1884, **45**, 270), "On Calcium Hydrosulphides," and by Divers (*ibid.*, 696), "The Origin of Calcium Thiosulphate: an Emendatory Note to a Paper on the Calcium Hydrosulphides," have proved of great assistance in the study of these oxidation changes of ammonium hydrosulphide. The author is in entire agreement with Divers' remarks on the origin of calcium thiosulphate, as contained in the emendatory note, these being in accord with the present experience.

At this stage it was evident that in order to follow out quantitatively the oxidation changes of solutions of ammonium sulphide, a special study of the various components was necessary.

This entailed the preparation of the hydrosulphides, sulphides, polysulphides, sulphite and thiosulphate of ammonium in a state of purity. The difficulties of analysis and procedure, and the poisonous nature of the gases evolved, probably account for the fact that no work on these compounds has been published since the appearance of the papers by Fritzsche (*J. pr. Chem.*, 1841, **24**, 460; *ibid.*, 1844, **32**, 313).

It is claimed by the author that, with the exception of ammonium pentasulphide obtained by Fritzsche, none of the ammonium sulphides or polysulphides have previously been prepared in the pure state, or the experimental conditions for their production been investigated.

It should be noted that great care must be taken to avoid inhalation of the vapours of ammonium sulphur compounds, as marked physiological effects are produced, even when small quantities are present in the air respired. Vapours of the ammonium sulphides produce much more serious effects than hydrogen sulphide, the toxic effect being greater in proportion to the volatility of the sulphide; the most dangerous compound is the volatile oily liquid of the composition, $(NH_4)_2S,2NH_3$.

II. *Analytical Methods employed.*

Experiment soon showed that no pure preparation of any of the ammonium sulphur compounds was available as a control, so that it became necessary to make a series of analyses of solutions to determine whether concordant results could be obtained. The rapidity with which these compounds undergo change on exposure to air renders it necessary to pay close attention to experimental detail, in order to obtain accurate analytical results. This is especially noticeable in the case of polysulphide solutions.

Determination of Total Sulphur.—It is well known that barium sulphate exhibits a great tendency to carry down with it other salts, and in consequence, to obtain accurate results, it was found necessary to exclude, from the solutions, substances, either known to exercise a solvent action on barium sulphate or liable to be carried down with it during precipitation; care also had to be taken in adjusting the quantities of the reagents employed.

Among oxidising agents, an ammoniacal solution of hydrogen peroxide is greatly to be preferred, but unfortunately commercial samples of hydrogen peroxide contain impurities, such as sulphuric acid, phosphoric acid, nitrite, phosphate, alumina, &c., which might interfere with the results. Oxidation was consequently effected by means of acid or alkaline solutions of bromine, preferably a solution of sodic hypobromite, the process being conducted as follows.

Fifty c.c. of a solution of sodic hydroxide (100 grams NaHO dissolved in 1000 grams H_2O) are placed in a tolerably capacious beaker, and pure bromine added in slight excess. The sulphide or polysulphide solution, or crystals (containing about 0·6 gram of sulphur) are rapidly weighed in a small stoppered weighing tube, then quickly transferred to the beaker, and the tube rinsed repeatedly with water. In cases where contact with water decomposes the polysulphides, the film of sulphur deposited in the weighing tube is dissolved by bromine water, and washed into the beaker. The whole is well agitated in the cold until the finely divided sulphur first precipitated is dissolved, and the solution is then gently warmed for some hours on a sand bath. Great care must be taken to prevent precipitation of sulphur, which, assuming the globular form, is only very slowly acted on by the bromine. When complete solution is effected, sufficient hydrochloric acid is added to decompose the excess of hypobromite, and the bromine is expelled by heat.

In the meantime the determination of ammonium is made, using standard sulphuric acid, and from this the approximate quantity of barium chloride required to effect precipitation could be calculated. The required quantity of hot barium chloride solution (containing 10 per cent. $BaCl_2,2H_2O$) is then run in, and the beaker and contents allowed to stand over-night. The precipitate and filter paper must be ignited separately, and the ash treated with a few drops of bromine water, and again ignited before adding it to the main portion. With these precautions, the barium sulphate is always pure, and the results are entirely satisfactory. Where bromine in acid solution is used as the oxidising agent, the same routine is followed, with one exception; before adding barium chloride, the solution is neutralised with ammonia, and then rendered slightly acid with hydrochloric acid.

It is unnecessary to expel all the bromine by evaporating the solution nearly to dryness before adding the barium chloride (see Lucion, *Chem. Zeit.*, 1888, **12**, 427, and G. Tauber, *ibid.*, 477; I can confirm their results).

Determination of Polysulphide Sulphur.—The solution or the crystals are rapidly transferred to a small stoppered weighing tube and the weight determined; the solution is then washed into a beaker containing a slight excess of dilute hydrochloric acid containing no free chlorine. The beaker, loosely covered, is then gradually heated upon a sand bath until no more hydrogen sulphide is evolved. The liquid is allowed to cool, and oxidation of the sulphur is effected by bromine, in the manner previously described.

As already noticed, solutions containing tetrasulphide or higher sulphides always deposit sulphur in the weighing tube during the process of dilution and transference to the beaker; this is dissolved in bromine water and added to the oxidising mixture in the beaker. The determinations of polysulphide sulphur made in this manner are accurate. According to the older methods, the sulphur, present as sulphide and polysulphide, is precipitated by a zinc salt; the precipitate is boiled with acid, and the residue of sulphur is oxidised and determined as barium sulphate. Amongst other disadvantages, the results were invariably high, owing to the precipitated barium sulphate retaining zinc salt.

Determination of Ammonium.—Since the determination of the ammonium as a platinochloride involved the sacrifice of much time, the following method was adopted, giving the ammonium value rapidly.

Standard solutions of normal and N/10 sulphuric acid were prepared, and also a N/10 solution of potassium hydroxide. The solution to be analysed was rapidly weighed, washed into a flask containing excess of the standard acid, and then heated and maintained at the boiling point until hydrogen sulphide ceased to be evolved, the excess of acid in the hot solution being determined by the standard alkali, using litmus as indicator. This method gives very accurate results, and a complete determination can be effected in less than half an hour. When a polysulphide is treated in the manner described, the sulphur which is deposited coagulates when the acid solution is boiled, and settles to the bottom of the flask; its presence does not, however, in any way interfere with the determination of the point of neutrality.

Time is saved if methyl-orange be employed as indicator, it being unnecessary to expel the hydrogen sulphide by boiling, but the results are not quite so accurate; using this method, the weighed sulphide solution is washed into a flask containing cold water, methyl-orange is added, and standard acid run in until the characteristic colour change is observed. As, however, the evolution of hydrogen sulphide during the titration is objectionable, it is better to employ the process first mentioned.

III. *Preparation of Solution of Ammonium Hydrosulphide.*

Compounds formed on passing Hydrogen Sulphide through a concentrated solution of Ammonia (*sp. gr.* 0·880).—A strong solution of ammonium hydrosulphide being required for the preparation of the ammonium polysulphides as decribed by Fritzsche (*J. pr. Chem.*, 1841, **24**, 460; 1844, **32**, 313), the method generally recommended was employed.

A current of washed hydrogen sulphide was passed through 300 c.c. of strong ammonia solution* (sp. gr. 0·880) for 18½ hours, the vessel containing the liquid being surrounded by cold water. When hydrogen sulphide escaped freely from the outlet tube, a portion of the solution was analysed. It was found to contain S = 27·75 and 27·66 per cent., NH_4 = 20·33 and 20·30 per cent.

A solution of ammonium hydrosulphide would require 36 11 per cent. sulphur to 20 3 of ammonium. The solution obtained being deficient in sulphur to the extent of 8·4 per cent., it was inferred that saturation was not complete.

A second similar experiment was made, but the stream of gas was maintained for 24 hours after the gas ceased to be absorbed. Analysis gave S = 28·11 and 28·20 per cent. NH_4 = 22·47 and 22·40 per cent. A solution of ammonium hydrosulphide of this strength requires 39·91 per cent. of sulphur.

These experiments prove:—

(*a.*) That strong ammonia solutions do not absorb the amount of hydrogen sulphide necessary for the complete conversion of the ammonia into ammonium hydrosulphide.

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* Throughout this paper the expression "strong ammonia solution" refers to "Liq. Ammon. Fortiss., sp. gr. 0·880."

(*b.*) That the stronger the solution of ammonia the less sulphur relatively is taken up.

In the first experiment, the end product contains 20·3 per cent. ammonium and 76·7 per cent. of the sulphur required to form $NH_4{\cdot}HS$. In the second experiment, the end product contains 22·47 per cent. ammonium and only 71·2 per cent. of the sulphur required to form $NH_4{\cdot}HS$.

In order to determine the nature of the product obtained on saturating a solution of ammonia (sp. gr. 0·880) with hydrogen sulphide, a portion of the solution was cooled by a freezing mixture of ice and salt. Leaf-like crystals were deposited which, after being drained as completely as possible from the mother liquor, were allowed to dissolve in their water of hydration, dissolution being aided by placing the bottle in slightly warm water. On standing, this clear solution deposited crystals; these on analysis gave $S = 30{\cdot}08$ per cent.; $NH_4 = 22{\cdot}62$ per cent.

For $NH_4{\cdot}HS$, 40·21 per cent. of sulphur would be required; the crystals, therefore, contain only three-quarters the amount of sulphur required by the formula $NH_4{\cdot}HS$, and their composition may be represented as $(NH_4)_2S,2NH_4{\cdot}HS$. A saturated aqueous solution of this substance contains 52·7 per cent. of the compound.

From this it is seen that the product obtained on saturating solution of ammonia (sp. gr. 0·880) with hydrogen sulphide at the ordinary temperature is not $NH_4{\cdot}HS$ but $(NH_4)_2S,2NH_4{\cdot}HS$.

A solution of $(NH_4)_2S,2NH_4{\cdot}HS$ cooled to 0° absorbs hydrogen sulphide, and fern-like crystals are deposited. After complete saturation at 0°, analyses were made of the crystals and of the mother liquor.

The mother liquor gave $S = 27{\cdot}01$ and 27·53 per cent.; $NH_4 = 17{\cdot}73$ per cent. and 17·75 per cent., corresponding to the formula $(NH_4)_2S,6NH_4{\cdot}HS$, for which 17·74 per cent. NH_4 requires 27·60 per cent. S.

A solution of the crystals gave $S = 23{\cdot}11$ and 23·16 per cent.; $NH_4 = 14{\cdot}03$ and 14·00 per cent., corresponding to the formula $(NH_4)_2S,12NH_4{\cdot}HS$, for which 14·0 per cent. NH_4 requires 23·12 per cent. S.

When washed hydrogen sulphide was passed into ammonia solution of sp. gr. 0·880 kept at 0°, white crystalline scales began to form on the surface of the liquid after the lapse of a considerable time; the current of gas was maintained until no further formation of crystals was observed, the flask being now half full of white crystalline plates resembling potassic chlorate in appearance. Analyses were then made of the mother liquor and of the crystals.

The mother liquor, which effervesced freely, was found to contain $(NH_4)_2S,6NH_4·HS$.

The crystals bore pressure between filter paper, being hard and crisp to the touch, a marked contrast to the behaviour of the compound $(NH_4)_2S,12NH_4·HS$ under similar circumstances. The values obtained were $S = 57·47$ per cent.; $NH_4 = 34·13$ and $34·05$ per cent., corresponding to the formula $(NH_4)_2S,18NH_4·HS + 4H_2O$, which requires $S = 57·47$; $NH_4 = 34·02$ per cent.

From these experiments, it is seen that the current statement that an aqueous solution of $NH_4·HS$ is obtained by saturating $NH_3 + Aq$ with hydrogen sulphide in absence of air, is only true when the value of Aq is defined. If $NH_3 + Aq$ be interpreted as solution of ammonia of sp. gr. 0·880, then in no case can a solution of $NH_4·HS$ be obtained on passage of H_2S. In its place a number of compounds are obtained to which the general form $(NH_4)_2S,xNH_4·HS$ may be given.

Experiments made to determine at what degree of Dilution, if any, $NH_4·HS$ is formed on saturating Solution of Ammonia with Hydrogen Sulphide.

The foregoing experiments indicated the probability that *in dilute solutions of ammonia* the amount of hydrogen sulphide requisite for the formation of ammonium hydrosulphide might be absorbed. This was proved to be the case, for on making a dilute solution in ice-cold water of the crystals $(NH_4)_2S,12NH_4·HS$, and passing a current of hydrogen sulphide for 24 hours through the solution cooled at 0°, analysis showed that the ammonium and sulphur in the solution were in the proportion required by the formula $NH_4·HS$.

Experiments were now made to determine at what degree of dilution $NH_4·HS$ is formed on saturating ammonia solution with

Solutions Cooled to 0° and Saturated with Hydrogen Sulphide.

	Degree of dilution.		Results of analysis of saturation product.		Percentage of S in saturation product. S in $NH_4·HS$ = 100.	Composition of saturation product.
	Vols.: 0·88 ammonia solution.	Vols.: Water.	NH_4 per cent.	S per cent.		
No. I	3	1	17·26; 17·30	25·11; 25·06	81·6	$(NH_4)_2S,4NH_4·HS$
" II	2	1	15·41; 15·51	24·75; 25·01	90·1	$(NH_4)_2S,8NH_4·HS$
" III	1	1	11·97; 11·94	19·16; 19·08	90·0	$(NH_4)_2S,8NH_4·HS$
" IV	1	2	8·99; 8·96	15·18; 15·20	95·0	$(NH_4)_2S,18NH_4·HS$
" V	1	3	7·15; 6·93	11·89; 11·80	95·2	$(NH_4)_2S,18NH_4·HS$
" VI	1	4	5·63; 5·64	9·93	100·0	$NH_4·HS$
" VII	1	5	4·98; 4·91	8·67; 8·66	100·0	$NH_4·HS$

hydrogen sulphide. The results are, for convenience, appended in the tabular form.

It appears from these experiments that ordinary strong solution of ammonia must be diluted with about four times its volume of water before the full amount of hydrogen sulphide required to form ammonium hydrosulphide is absorbed. The strongest solution of ammonium hydrosulphide contains less than 19 per cent. $NH_4\cdot HS$ (see Experiment V). The solution obtained when the dilution was 1 : 4 (see Experiment VI) contained 16 per cent. $NH_4\cdot HS$. The strongest solution of ammonium hydrosulphide obtainable contains, therefore, between 16 and 19 per cent. of $NH_4\cdot HS$.

Attempts to prepare Ammonium Hydrosulphide in the Solid State.

It is stated on the authority of Bineau (*Ann. Chim. Phys*, 1838, **67**, 230; 1838, **68**, 435) that, at ordinary temperatures, hydrogen sulphide and gaseous ammonia combine in equal volumes in whatever proportions they may be mixed. The compound crystallises in colourless needles and scales, and volatilises and sublimes, even at ordinary temperatures; it has a penetrating odour of ammonia and of hydrogen sulphide, and an alkaline action; rapidly turns yellow on exposure to the air, from formation of pentasulphide of ammonium (Thénard); it yields a colourless solution with water. As no analyses of this compound are given, it was determined to repeat the experiment. A wide-mouth bottle was fitted with a cork and two glass tubes to serve as inlets for the hydrogen sulphide and ammonia respectively, whilst a third tube served as an outlet for the escape of gases On passing the gases, ammonia being in excess, into the bottle cooled with ice, colourless needles and scales were formed; but the greater portion was deposited on the sides of the bottle as a white, porcelain-like mass.

Attention was directed especially to the question, is $NH_4\cdot HS$ the only product obtained? In order to test this point, ice-cold water was introduced into the bottle containing the white crystalline solid; three solutions were made in rapid succession and numbered I, II, and III, No. I being the weakest, and No. III the strongest.

The crystals being assumed to be $NH_4\cdot HS$, analysis of the solutions should show either that all three had the same composition as the crystals, that is, $NH_4\cdot HS$, showing that ammonium hydrogen sulphide when *once formed* will yield concentrated aqueous solutions without loss of hydrogen sulphide, or that, as previously experienced, the existence of $NH_4\cdot HS$ as such, in concentrated aqueous solutions, is not possible, hydrogen sulphide being evolved.

The results of the analysis of the three solutions are given below.

	NH_4 per cent.	S per cent.	Percentage of S present. S in $NH_4{\cdot}HS$ = 100
Solution No. I..........	3·95	6·0	87·5
„ No. II.........	8·55	13·48	88·4
„ No. III........	16·10	22·87	79·7

These analyses show that the crystals obtained were not pure $NH_4{\cdot}HS$, as the solution No. I, which is within the dilution limit previously determined for $NH_4{\cdot}HS$ (see p. 286), had not this composition, but contained only 88 per cent. of the sulphur required for $NH_4{\cdot}HS$. From this it is evident that, contrary to Bineau's statement (*loc. cit.*), it is not a matter of indifference whether the volumes of the gases are adjusted or not.

A second preparation was therefore made, in which the hydrogen sulphide was kept in slight excess, the other details being similar to those of the preceding experiment. The crystals thus formed were not to be distinguished in appearance from those obtained in the previous experiment; on analysis, however, they proved to be $NH_4{\cdot}HS$, the analysis of the solution of the crystals giving NH_4 = 6·23 per cent., S = 10 57 per cent., corresponding to

$$(NH_4)_2S,18NH_4{\cdot}HS,$$

derived from the action of water on $NH_4{\cdot}HS$, the solution being too concentrated for the existence in it of $NH_4{\cdot}HS$ (see p. 286).

Ammonium hydrosulphide can, therefore, be prepared in a state of purity by this method, if the volumes of the gases are equal, or if the hydrogen sulphide is in slight excess, but not if the ammonia is in excess.

Only one other method is given for the preparation of ammonium hydrosulphide, namely, by passing hydrogen sulphide into an alcoholic solution of ammonia.

To investigate this method, absolute alcohol was saturated with dry ammonia, and washed hydrogen sulphide was passed into the alcoholic solution kept at 0°. The large, white, micaceous plates which formed were separated from the mother liquor, and the crystals dried by pressure between filter-paper. The odour exhaled is almost insupportable.

Analyses were made of the crystals and of their solutions in water. The conclusions arrived at are :—

1. This method does not yield $NH_4{\cdot}HS$, but substances containing less sulphur than is required by the formula $NH_4{\cdot}HS$.

2. These substances are of the same nature as those obtained on saturating aqueous solutions of ammonia with hydrogen sulphide,

$(NH_4)_2S,xNH_4 \cdot HS$. The product obtained from alcoholic solution varies according to the strength of the solution.

3. The crystals obtained contain alcohol.

IV. *Ammonium Monosulphide.*

Experiments were now made with the view of ascertaining whether a strong ammonia solution, when supplied with the amount of hydrogen sulphide required to form $(NH_4)_2S$, would yield a solution of this substance, or whether the product would behave as a mixture of ammonia and one of the compounds of the type $(NH_4)_2S,xNH_4 \cdot HS$ previously described. The usual method for preparing a solution of ammonium monosulphide, namely, to divide a quantity of aqueous ammonia into two equal parts, saturate one with hydrogen sulphide, and then add the other to it, is useless for making a concentrated solution, as the compound will contain an excess of ammonia. To determine the ammonia and sulphur in the portion saturated, and then to add the required quantity of titrated ammonia solution, is open to the objection that the product obtained on saturation of 0·880 ammonia solution, *e.g.*, $(NH_4)_2S,2NH_4 \cdot HS$, might not be acted on by the ammonia added, and the two would then exist separately in the solution.

The other method for making the solution, namely, to pass hydrogen sulphide in quantity just sufficient to form ammonium monosulphide, entails analysis of the solution at intervals, in order to guard against the introduction of excess of hydrogen sulphide. It is evident that a rapid and accurate method of determining when the monosulphide limit has been reached is required.

Divers and Shimidzu (Trans., 1884, 45, 275) have employed manganous salts for the detection of basylous hydrogen in such cases, the test being based upon the following reactions,

$$(NH_4)_2S + MnSO_4 = MnS + (NH_4)_2SO_4,$$
$$2NH_4 \cdot HS + MnSO_4 = MnS + (NH_4)_2SO_4 + H_2S,$$

half the sulphur present as hydrosulphide escaping precipitation, and appearing as hydrogen sulphide. This method, however, has not proved satisfactory in the author's hands, owing to the fact that the reaction does not take place sharply. The test is made by adding the solution to be examined to an excess of a solution of a manganous salt, contained in a stoppered glass cylinder, which is then closed and shaken, and, after an interval, a piece of lead paper is introduced into the air in the cylinder. It was found, however, that, even when the ammonia was in excess, some time elapsed before the air was free from hydrogen sulphide, and as the solution approaches the monosulphide limit, it is difficult to determine whether the hydrogen sulphide in the air arises from undecomposed ammonium monosulphide or is due to the presence of hydrosulphide. A magnesium salt is recommended for the detection of excess of ammonia, but the reagent proved to be useless, as the presence of ammonium sulphide prevents the precipitation of magnesium hydroxide.

These difficulties have been overcome by employing a solution of cupric sulphate, and it is possible by its use to determine qualitatively or quantitatively any excess, either of ammonia or of hydrogen sulphide, over and above that required to form ammonium monosulphide. The following reactions may occur.

(*a.*) $2CuSO_4 + 2NH_4{\cdot}HS = 2CuS + (NH_4)_2SO_4 + H_2SO_4$.

(*b.*) $CuSO_4 + (NH_4)_2S = CuS + (NH_4)_2SO_4$.

(*c.*) $2CuSO_4 + (NH_4)_2S + 2NH_4HO = CuS + Cu(HO)_2 + 2(NH_4)_2SO_4$.

The examination is made as follows. An excess of solution of recrystallised cupric sulphate (1 c.c. = about 0·1 gram $CuSO_4$) is placed in a flask, water is added, and the solution to be examined is run in. The flask is closed by a tightly-fitting cork, and the flask and contents shaken; the reaction is very sharp, and the air in the flask, after once shaking, is invariably free from hydrogen sulphide. The supernatant liquor is filtered, and the precipitate remaining in the flask is washed with hot water by decantation until free from acidity and copper salt. The filtrate is allowed to cool, and titrated with decinormal solution of potassic hydroxide. If the first drops produce a turbidity, showing that the mixture has not become acid, ammonia solution is added to the precipitate remaining in the flask, which is well shaken. On filtering, a deep blue solution is obtained, showing that an excess of ammonia over that required to form ammonium monosulphide was present. A solution containing ammonia and hydrogen sulphide in the exact proportions required by ammonium monosulphide develops no acidity, and the precipitate, after treatment with ammonia, does not yield a blue filtrate.

To determine any excess of ammonia quantitatively, it is only necessary to add to the cupric sulphate solution in the flask an excess of standard acid, and to proceed as above, the difference between the acid taken and that found by titration corresponding to the excess of ammonia present. The reagent is specially valuable for the examination of polysulphide solutions, and gives accurate results when used quantitatively. The determinations of the sulphur in commercial samples of ammonium hydrosulphide can be rapidly effected by this method.

Being now in a position to determine readily when the amount of hydrogen sulphide required to form ammonium monosulphide had been taken up, a solution was made by passing a current of washed hydrogen sulphide through a strong solution of ammonia, cooled to 0°. Test samples were taken from time to time, and treated with cupric sulphate solution, and when the neutral point was reached the solution was analysed in the usual way, the following values being obtained, $NH_4 = 25{\cdot}88$ and $25{\cdot}95$ per cent., $S = 22{\cdot}91$ and $22{\cdot}80$ per cent. This is in the proportion required by ammonium monosulphide. For $(NH_4)_2S$ the ammonium found would require $S = 23{\cdot}02$ per cent.

An attempt to obtain crystals by cooling the solution even at —40° was unsuccessful, but it is worthy of note that in all cases where free ammonia was present it exercised a great solvent power, tending to prevent the deposition of crystals. Is then the solution which gives analytical results pointing to $(NH_4)_2S$ a solution of this substance, or is it to be regarded as a mixture of a compound of the type $(NH_4)_2S,xNH_4{\cdot}HS$ with $xNH_4{\cdot}HO$? If the solution be saturated with hydrogen sulphide, the compound formed has the composition $(NH_4)_2S,2NH_4{\cdot}HS$, and crystals of this substance can be obtained from it; that is to say, the supposed solution of $(NH_4)_2S$ only takes up half the amount of hydrogen sulphide required to form $NH_4{\cdot}HS$.

On diluting the original solution with varying quantities of water, and then passing hydrogen sulphide to saturation, the amount of the gas absorbed does not progressively increase with the dilution, but solutions of the composition $(NH_4)_2S,4NH_4{\cdot}HS$, $(NH_4)_2S,8NH_4{\cdot}HS$, $(NH_4)_2S,18NH_4{\cdot}HS$, and, finally, $NH_4{\cdot}HS$ are obtained.

The amount of hydrogen sulphide absorbed always corresponds with one of these compounds, and no intermediate ratios are obtained. For example, the solution $(NH_4)_2S,8NH_4{\cdot}HS$ will not absorb more hydrogen sulphide on progressive dilution; when, however, a certain stage of dilution is reached absorption once more takes place, and a solution of the compound $(NH_4)_2S,18NH_4{\cdot}HS$ can be obtained.

On the assumption that only the compounds $(NH_4)_2S$ and $NH_4{\cdot}HS$ exist, and that the amount of hydrogen sulphide absorbed depends on the amount of the $(NH_4)_2S$, which is dissociated, it seems impossible to explain why only solutions corresponding with the compounds above mentioned can be obtained.

On the other hand, it is easy to understand the process of absorption of hydrogen sulphide, if the existence of definite compounds of the type $(NH_4)_2S,xNH_4{\cdot}HS$ be admitted. Crystals of the composition $(NH_4)_2S,2NH_4{\cdot}HS$, $(NH_4)_2S,12NH_4{\cdot}HS$, $(NH_4)_2S,18NH_4{\cdot}HS$ have actually been obtained.

Moreover, if crystals of $NH_4{\cdot}HS$ be treated, in a stoppered bottle, with water, then—if the quantity of water be less than is required for a solution of $NH_4 \cdot HS$, as found by direct saturation (see table, p. 285)—an evolution of hydrogen sulphide is observed: a point of stability being reached when the solution corresponds with the compound of the type $(NH_4)_2S,xNH_4 \cdot HS$ possible at the degree of dilution.

The explanation of the observed facts offered by the author is as follows. When hydrogen sulphide is passed into ammonia solution $(NH_4)_2S$ is first formed, and this breaks down giving $NH_4 \cdot HS$ and $NH_4 \cdot HO$. The $NH_4 \cdot HS$ thus produced unites with more $(NH_4)_2S$ to form compounds of the general formula $(NH_4)_2S,xNH_4 \cdot HS$, the value of x increasing with the dilution of the solution. With the strongest ammonia solution, the saturated product has the composition $(NH_4)_2S,2NH_4 \cdot HS$, and when the saturated solution contains only about 6 per cent. of ammonium, the full amount of hydrogen sulphide required to form $NH_4 \cdot HS$ is absorbed. Within certain tolerably wide limits of dilution, the value of x remains constant, and the solutions do not progressively take up more hydrogen sulphide (see table, p. 285).

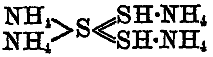
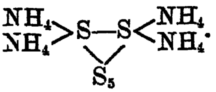
Even if the current of hydrogen sulphide be not continued to complete saturation of the solution, the product corresponding to the dilution alone will be formed, the excess of ammonia remaining free; thus (*vide* p. 296) the solution yielding analytical figures for $(NH_4)_2S$ is to be regarded as one of $(NH_4)_2S,2NH_4 \cdot HS + 2NH_4 \cdot HO$. Thus, although neither $NH_4 \cdot HS$ nor $(NH_4)_2S$ exist as such in concentrated solutions, the two combine together, forming compounds of considerable stability, their solutions being incapable of taking up more hydrogen sulphide until they are furthur diluted. The crystals of $(NH_4)_2S,18NH_4 \cdot HS$ which have been obtained are well defined and are fairly stable. This view of the constitution of the supposed solution of ammonium monosulphide—namely, that it is a mixture of $(NH_4)_2S,2NH_4 \cdot HS + 2NH_4 \cdot HO$—receives ample experimental confirmation. In the first place, its behaviour with solution of cupric sulphate is intelligible. Secondly, the failure of the solution to yield crystals by cooling can be attributed to the known solvent action exercised by free ammonia. In the third place, the solution exhibits no tendency to dissolve sulphur in the simple fashion attributed to the monosulphide, thus—

$$(NH_4)_2S + S_1 \ldots . S_2, \&c., = (NH_4)_2S_2 \ldots . S_3, \&c.$$

On the contrary, as is described later, the solution, when treated in the cold with finely-divided sulphur, evolves hydrogen sulphide, and when rather more sulphur has gone into solution than is required to form $(NH_4)_2S_2$, a crystalline compound is obtained which has invariably the composition of tetrammonium heptasulphide, $(NH_4)_4S_7$, in which five of the sulphur atoms are not in direct union with ammonium.

The formation of this compound is intelligible, if the composition of the supposed ammonium monosulphide solution be

$$(NH_4)_2S,2NH_4{\cdot}HS + 2NH_4{\cdot}HO.$$

On treating the compound  $\begin{matrix}NH_4\\NH_4\end{matrix}\!>\!S\!<\!\begin{matrix}SH{\cdot}NH_4\\SH{\cdot}NH_4\end{matrix}$ with sulphur, H_2S is eliminated, giving rise to two molecules of diammonium monosulphide $(NH_4)_2S$, which by combination with five atoms of sulphur form the compound $(NH_4)_4S_7$, thus  $\begin{matrix}NH_4\\NH_4\end{matrix}\!>\!S{-}S\!<\!\begin{matrix}NH_4\\NH_4\end{matrix}$ with S_5 bridging the two S atoms.

V. *Preparation of Crystals of Ammonium Monosulphide.*

Since the strong solution just described does not behave like one of ammonium monosulphide, and as no crystals of monosulphide could be obtained from the solution, an attempt was made to obtain crystals of the monosulphide by the union of the dry gases.

The method given by L. Gmelin (*Handbook of Chemistry*, **2**, 451) is to pass a mixture of one volume of hydrogen sulphide with rather more than two of ammonia into a tube cooled down to −18°. It is also stated that at ordinary temperatures the two gases combine in equal volumes only, even when the ammonia is present in large excess. (The latter statement has been shown to be incorrect, see p. 287.)

These statements rest on the authority of Bineau (*Ann. Chim. Phys.*, 1839, **70**, 261). He passed a mixture of 6·7 c.c. H_2S with 14·8 c.c. NH_3 through a tube cooled by a mixture of ice and salt, and measured the uncondensed gas (1·2 c.c.), which he regarded as ammonia; from this he concluded that two volumes of ammonia had combined with one volume of hydrogen sulphide; it was found that the monosulphide formed gave off ammonia on being removed from the freezing mixture, leaving ammonium hydrosulphide. As only about 20 milligrams of the solid could have been obtained by Bineau, it was thought advisable to repeat the experiment so as to obtain sufficient of the compound for analysis.

The apparatus employed was the same as that used for the preparation of ammonium hydrosulphide in the solid state (see p. 286). The bottle was cooled by ice and salt, and was kept in the freezing mixture for half an hour before the ammonia and hydrogen sulphide were admitted; these were dried by passing them through drying towers and tubes containing quicklime and calcium chloride respectively; and the air in the bottle was displaced by ammonia before the hydrogen sulphide was admitted, and the rate at which the gases were passed in was so adjusted that the ammonia was considerably in excess. The product obtained was evidently not homogeneous; glittering, micaceous crystals, resembling naphthalene in appearance, were formed, and at the same time a white, porcelain-like solid was deposited in the bottle, which subsequent experience showed to be ammonium hydrosulphide (see Bineau, *loc. cit.*). The crystals deposited at the neck of the bottle, where the temperature was not quite so low, evolved gas copiously (? NH_3), leaving a crystalline residue (? $NH_4{\cdot}HS$), and a third substance was also observed in fern-like crystals, apparently one of the compounds $(NH_4)_2S,xNH_4{\cdot}HS$ previously described.

On removing the bottle from the freezing mixture, the micaceous crystals decomposed with great rapidity, torrents of ammonia being evolved; water was added, when the remaining crystals dissolved with great ease, the porcelain-like mass, $NH_4{\cdot}HS$, dissolving more slowly. The solution poured off from the undissolved hydrosulphide, and subjected to analysis, showed that the greater proportion of the mass consisted of $NH_4{\cdot}HS$. The experiment was repeated, using the same apparatus, but with the addition of two U-tubes, which were also kept at −18°, and the ammonia was passed in greater excess. The micaceous crystals were obtained without difficulty, and presented a most beautiful appearance, reflecting a bluish-white light; but the total yield was disappointingly small. Ammonium hydrosulphide was also observed, but the fern-like crystals were not formed. On inspecting the cooled U-tubes connected with the outlet tube of the bottle, it was found that a yellowish, heavy liquid had condensed in the one next the bottle; this liquid was highly refractive, resembling carbon bisulphide in this respect. A few drops of this oily liquid had also collected in the second U-tube. On removing the tube from the freezing mixture, the liquid boiled violently, evolving torrents of ammonia, and leaving a white, crystalline residue, which, in turn, decomposed with evolution of ammonia; the final residue appeared to consist of ammonium hydrosulphide. The liquid product, therefore, was richer in ammonia than any sulphide yet obtained; it appears to have been formed by the passage of the excess of ammonia over the crystals of ammonium monosulphide deposited in the bottle, and was subsequently condensed in the U-tubes. Some of this substance was doubtless formed in the previous experiment, but escaped uncondensed; this would account for the serious symptoms experienced during the first preparation by the author and his assistant. When ice-cold water was added to the oily liquid before removing the U-tube from the freezing mixture, some ammonia was given off; the solution, which was of a light straw colour, when submitted to analysis, gave $NH_4 = 3{\cdot}56$ and $3{\cdot}52$ per cent.; $S = 1{\cdot}67$ per cent. These figures show that the oily liquid contains twice as much ammonia as ammonium monosulphide does, its composition being represented by the formula $(NH_4)_2S,2NH_3$. The excess of sulphur found, 1·67 per cent. as against 1·60 theory, is accounted for by the loss of ammonia during solution in water, and in the subsequent operations. A third experiment similar to the one just described was now made with the object of obtaining crystals of ammonium monosulphide as far as possible free from ammonium hydrosulphide, and also more of the volatile oily liquid in a state of purity.

Some small quantity of ammonium hydrosulphide was formed, but, on introducing ice-cold water, the thin, micaceous plates rapidly passed into solution, leaving the porcelain-like mass of $NH_4{\cdot}HS$, which dissolved but slowly. The solution thus obtained, when analysed, gave $NH_4 = 14{\cdot}70$ per cent.; $S = 16{\cdot}50$ per cent.; $(NH_4)_2S$ requires, for the amount of NH_4 found, only 13·67 per cent. of sulphur.

This analysis shows that when the micaceous crystals are rapidly dissolved in ice-cold water, a solution is obtained in which the proportions of ammonium and sulphur are approximately those required by ammonium monosulphide.

A strong solution of the oily liquid was made with ice-cold water before removing the U-tube from the freezing mixture. The evolution of ammonia was again observed, and the solution was therefore diluted with about twice its volume of ice-cold water, to increase its stability. An analysis of the diluted solution gave $NH_4 = 12{\cdot}53$ and 12·48 per cent.; $S = 6{\cdot}16$ and 6·25 per cent.; for $(NH_4)_2S,2NH_3$, the NH_4 found requires $S = 5{\cdot}55$ per cent.

This confirms the experience, that on making the first concentrated aqueous solution of the oily liquid in the U-tube there is loss of ammonia, this loss being due to insufficient dilution.

To the present statements concerning ammonium monosulphide must be added these facts.

1. Passing dry ammonia and dry hydrogen sulphide into a bottle cooled to −18° does not yield ammonium monosulphide alone, even when the ammonia is in considerable excess. Ammonium hydrosulphide is also formed, but by carefully adjusting the volumes of the gases and the rate of flow, ammonium monosulphide can be obtained in the form of micaceous crystals. When these crystals are rapidly dissolved in ice-cold water, a solution is obtained approximating sufficiently closely to the composition $(NH_4)_2S$ to justify the conclusion that the micaceous crystals are ammonium monosulphide. This view is also supported by the behaviour of the crystals when the temperature rises, ammonia being copiously evolved and a residue of ammonium hydrosulphide left.

2. If the ammonia is largely in excess, then a more volatile sulphide is obtained, containing more ammonia than ammonium monosulphide, and having the composition $(NH_4)_2S,2NH_3$.

VI. *The Polysulphides of Ammonium.*

Our knowledge concerning the polysulphides of ammonium is mainly based on the work of Fritzsche, as detailed in his two papers—"On Two Crystalline Compounds of Ammonium with Sulphur" (*J. pr. Chem.*, 1841, **24**, 460), "On Tetrasulphide of Ammonium" (*ibid.*, 1844, **32**, 313). A condensed, but not wholly accurate, account of Fritzsche's work is given in *Watt's Dict.* (new edition), I, 204.

Fritzsche claims to have obtained diammonium tetrasulphide, pentasulphide, and heptasulphide; his results will be criticised in the portions of this paper which deal with the preparation of these salts.

Fritzsche's attempt to prepare diammonium trisulphide and disulphide, by continued treatment of the mother liquor, from which he claimed to have obtained the tetrasulphide, resulted in failure. The mother liquors from which the diammonium pentasulphide and tetrasulphide had crystallised were not analysed by him.

Diammonium Pentasulphide.—The investigation of the products formed when aqueous ammonia is saturated with hydrogen sulphide, showed that the solution Fritzsche employed as his starting point for the preparation of diammonium pentasulphide, which he believed to contain ammonium hydrosulphide, could not have had that composition. Most probably it was made by saturating strong ammonia solution with hydrogen sulphide, in which case the product, if completely saturated, would have been of the approximate composition $(NH_4)_2S,2NH_4{\cdot}HS$, and if incompletely saturated, the composition $(NH_4)_2S,2NH_4{\cdot}HS,xNH_4{\cdot}HO$, that is approximating to ammonium monosulphide. Under these circumstances it was considered preferable to act with sulphur on a solution containing the ammonium and sulphur in the ratio $2NH_4 : S$ (see p. 290). When a solution of about 40 per cent. concentration was warmed with excess of sulphur, in the form of impalpable powder, the temperature being gradually allowed to rise to 80°, there was a very brisk action, hydrogen sulphide was evolved in quantity, and the sulphur dissolved rapidly, the solution appearing almost black. On cooling, crystals separated, but on attempting to dissolve them by the addition of water, the crystals were immediately decomposed, sulphur being deposited and a pale yellow solution obtained.

The following experiment with a more dilute solution was then made. 200 c.c of the 40 per cent. solution were placed in a flask, diluted with 75 c.c of water, and sulphur added in greater excess than would be required for the formation of diammonium pentasulphide;

the mixture was then gently warmed on a water bath, the temperature not being allowed to exceed 80°. As before, much hydrogen sulphide was evolved, the sulphur dissolved freely, and the liquid became deep red. When the action was complete, the liquid was poured off from the undissolved sulphur into a flask and left standing overnight. In the morning a crop of fine large yellow oblique prisms had formed; the crystals exhibiting the features noted by Fritzsche as characteristic of diammonium pentasulphide. The mother liquor was poured off from the crystals and reserved for analysis in closely stoppered bottles. The crystals were at once analysed, and gave NH_4 = 18·14 and 18·11 per cent.; S = 81·28 per cent. They are therefore anhydrous diammonium pentasulphide.

Calculated for $(NH_4)_2S_5$. S = 81·63; NH_4 = 18·37.

The mother liquor from the crystals of diammonium pentasulphide could not be a solution of $(NH_4)_2S_5$, as much hydrogen sulphide had been evolved during the action, and the mother liquor must consequently contain free ammonia. On cooling this mother liquor in a freezing mixture, a crystalline mass was deposited, which was rapidly washed with alcohol after the liquid portion had been poured off; on allowing the crystals to liquefy at a gentle heat, a solution of the substance in its own water of hydration was obtained, and there was no deposition of sulphur. On analysis it gave NH_4 = 9·35 and 9·32 per cent. Total S = 37·15 and 36·83 per cent. S as polysulphide = 28·67 and 28·67 per cent.

This analysis shows that the ratio S/NH_4 in this solution is 3·98. A pure solution of diammonium pentasulphide would give the ratio S/NH_4 = 4·44, and consequently the above preparation contains polysulphides lower than pentasulphide. Another preparation yielded precisely similar results. It is to be remarked here that the crystalline masses obtained on freezing, and which yielded the above solutions, had the composition $(NH_4)_2S_{4\cdot5}$ or $(NH_4)_4S_9$.

On cooling a portion of one of these solutions in a freezing mixture, crystals were deposited as usual, but, after the mother liquor had been poured off, they did not entirely dissolve on warming to 50°, as on previous occasions. These crystals were richer in sulphur than $(NH_4)_2S_5$, whilst the mother liquor had approximately the composition of diammonium tetrasulphide, $(NH_4)_2S_4$.

It was concluded, then, that at this stage the red liquors contained a series of polysulphides, probably diammonium heptasulphide, $(NH_4)_2S_7$; pentasulphide, $(NH_4)_2S_5$; tetrasulphide, $(NH_4)_2S_4$; and, possibly, disulphide, $(NH_4)_2S_2$.

Attempts to prepare Polysulphides by the Action of Reputed Solution of Diammonium Monosulphide on Sulphur in Sealed Tubes.

The method of preparation previously described being complicated, and involving loss of hydrogen sulphide, crystallisation, &c., it was thought that possibly the formation of a series of polysulphides might be due to this cause. It is generally stated that diammonium disulphide, $(NH_4)_2S_2$, is obtained when sulphur is dissolved in the monosulphide in the proportion $(NH_4)_2S : S$; experiments were, therefore, made to test the truth of this statement, as, if it were true, the higher polysulphides should be obtained by a similar process.

The solution used was one previously described (p. 290), which, whilst giving analytical results corresponding to those required for diammonium monosulphide, was, as previously stated, regarded with suspicion. It was, however, the only solution available for the purpose, and the preparation of diammonium disulphide, if effected previously, must have been made with a similar solution.

The method adopted was as follows. Quantities of 15 c.c. of the reputed solution of diammonium monosulphide (of known strength) were placed in glass tubes, and to each was added the calculated amount of sulphur for a definite polysulphide. The tubes were then sealed, and, with the exception of that for diammonium disulphide, $(NH_4)_2S_2$, placed in a capacious beaker containing cold water, the temperature of which was gradually raised. An evolution of gas was in each case observed where the sulphur was being dissolved. If the solution were one of diammonium monosulphide, this should not occur.

I. *Attempted formation of* $(NH_4)_2S_5$ [15 c.c. reputed $(NH_4)_2S$ solution + 11·22 grams S].—The sulphur was, at first, rapidly dissolved, afterwards more slowly, and then, whilst a considerable mass of sulphur was still undissolved, the solution suddenly solidified, a mass of small, needle-shaped crystals being obtained. On heating to 100°, a little more sulphur was dissolved, but as a large portion still remained undissolved, the tube was heated for three hours in an air bath at 120°. The sulphur melted, but no further action was observed. The solution was deep red, and almost opaque, when viewed by transmitted light; on cooling, a crystalline mass, mixed with sulphur, was deposited, which was useless for analysis.

In a second experiment with a more dilute solution, a still larger residue of sulphur remained undissolved, indicating that dilution was unfavourable to solution of the sulphur. These experiments showed that the power of dissolving sulphur, possessed by reputed solution of diammonium monosulphide, was greatly below the limits required to form diammonium pentasulphide; experiments were, therefore, made to prepare the lower members of the series.

II. *Attempted formation of* $(NH_4)_2S_2$ [15 c.c. reputed $(NH_4)_2S$ solution + 2·8 grams S].—A yellow solution was obtained from the commencement, the sulphur being almost completely dissolved in the cold; on warming slightly, a clear, reddish-yellow solution was obtained. There was no deposition of crystals at the ordinary temperature, but, on cooling with ice and salt, tufts of small, yellow needles separated after a time. There was no pressure on opening the tube. The crystals from the mother liquor were separated, rapidly dried between filter-paper, and transferred to stoppered weighing tubes. These crystals dissolved in water, giving a clear, yellow solution, which did not deposit sulphur for a considerable time. On analysis, the crystals gave S = 61·05, NH_4 = 19·68, H_2O (by difference) = 19·27 per cent.

Although the substance was obtained in well-formed crystals, its composition does not accord with any known ammonium sulphide; if they be represented by the formula $(NH_4)_4S_7,4H_2O$, tetrammonium heptasulphide, they should contain S = 60·88, NH_4 = 19·56, H_2O = 19·56 per cent.

III. *Attempted formation of* $(NH_4)_2S_3$ [15 c.c. reputed $(NH_4)_2S$ solution + 5·61 grams S].—On shaking in the cold, part of the sulphur dissolved, and then crystallisation took place.* On warming to 70—80°, an orange-red solution was obtained, which, after remaining for some time at the ordinary temperature, deposited rosettes of fine needles. After the crystals had been separated from mother liquor, as in the previous experiment, water was added in the usual course of analysis, when they were at once decomposed, sulphur being deposited.

The results of analysis show that the crystals are diammonium pentasulphide with $1H_2O$.

	S.	NH_4.	H_2O.
Calculated for $(NH_4)_2S_5,H_2O$..	74·77	16·82	8·41 per cent.
Found	74·79	16·94	(8·27) „

This salt differs from diammonium pentasulphide previously obtained (p. 296) in containing $1H_2O$. In form it is easily distinguished from the oblique prisms of the anhydrous pentasulphide, the monhydrated salt occurring in rosettes built up of fine-pointed needles. Both salts are decomposed rapidly by water, sulphur being deposited. This is noteworthy, as in *Watt's Dictionary of Chemistry* (Morley and Muir, 1, 204) it is stated that $(NH_4)_2S_5$, in the form of orange-red prismatic crystals, is easily soluble in water and alcohol, although

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* Later experiments proved this crystalline product to be $(NH_4)_4S_7$ tetrammonium heptasulphide.

Fritzsche states that the pentasulphide is decomposed by water yielding a lemon-coloured solution of a compound containing less sulphur whilst sulphur is deposited.

IV. *Attempted formation of* $(NH_4)_2S_4$ [15 c.c. reputed $(NH_4)_2S$ solution + 8·42 grams S].—The sulphur dissolved with difficulty, but solution was complete at about 80°, and a deep red solution was obtained which appeared black by reflected light. On cooling, crystallisation took place, very little mother liquor being left. The crystals were yellow needles. After the crystals had been separated, as in the previous experiments, the addition of water for the purpose of analysis decomposed them, sulphur being deposited.

The results of analysis show that the crystals are tetrammonium enneasulphide $(NH_4)_4S_9 + 3\frac{1}{2}H_2O$.

	S.	NH_4.	H_2O.	
Calculated for $(NH_4)_4S_9,3\frac{1}{2}H_2O$	68·08	17·02	14·90	per cent.
Found......................	68·35	16·98	(14·67)	„

The results of the preceding experiments are given in a tabular form to facilitate reference.

Table showing Results obtained by the Action of Reputed Ammonium Sulphide Solution on Sulphur in Sealed Tubes.

Attempted formation of	Proportions used of		Residue of sulphur.	Product.
	$(NH_4)_2S$ sol. c.c.	Sulphur (grams).		
$(NH_4)_2S_5$....	15	11·22	Large........	Solid mass of crystals mixed with sulphur.
$(NH_4)_2S_4$....	15	8·42	No residue, but S dissolves with difficulty	Solid mass of crystals of composition $(NH_4)_4S_9 + 3\frac{1}{2}H_2O$.
$(NH_4)_2S_3$....	15	5·61	None........	Crystals of $(NH_4)_2S_5 + H_2O$, the mother liquor separated containing lower sulphides.
$(NH_4)_2S_2$....	15	2·8	None........	Mother liquor separated. Crystals of $(NH_4)_4S_7 + 4H_2O$.

The following conclusions are drawn from the preceding experiments.

1. That the solution employed, giving analytical results corresponding with those required by diammonium monosulphide, is not in reality a solution of that substance.

2. That this solution is to be regarded as containing, not $(NH_4)_2S$ simply, but the compound $(NH_4)_2S,2NH_4{\cdot}HS + 2NH_4{\cdot}HO$.

3. That the lower polysulphides cannot be obtained by dissolving the calculated amount of sulphur in this solution.

4. That when sulphur acts on this solution, hydrogen sulphide is eliminated (which would not take place were the solution one of diammonium monosulphide) and two definite polysulphides are obtained, namely, $(NH_4)_4S_7$, tetrammonium heptasulphide, and $(NH_4)_4S_9$, tetrammonium enneasulphide.

5. In no case is more sulphur taken up than is required for the formation of the compound $(NH_4)_4S_9$.

Previous experiments seemed to show that the complex polysulphides obtained might be due to the constitution of the reputed $(NH_4)_2S$ solution, that is $(NH_4)_2S,2NH_4{\cdot}HS + 2NH_4{\cdot}HO$. When acted on by sulphur, $(NH_4)_2S,2NH_4{\cdot}HS$ parts with H_2S, and the residual group, $(NH_4)_4S_2$, is able to take up 5 and 7 atoms of sulphur respectively, forming the complex polysulphides $(NH_4)_4S_7$ and $(NH_4)_4S_9$. It appeared probable, therefore, that if sulphur were presented to diammonium monosulphide $(NH_4)_2S$ at the moment of its formation, the action would be simpler in its character, and that in this manner a solution of diammonium pentasulphide might possibly be obtained.

Preliminary experiments showed that if a tolerably concentrated solution of ammonia were treated with hydrogen sulphide in the presence of excess of sulphur, the latter was rapidly dissolved, the solution acquired the deep red colour characteristic of solutions of polysulphides, whilst no hydrogen sulphide escaped until sulphur ceased to be dissolved. An examination of the product showed that no oxidised sulphur was present, and that it contained neither free ammonia nor ammonium hydrosulphide. This new method of preparing polysulphide liquors was consequently adopted in all subsequent experiments. Attempts were now made to prepare a solution of diammonium pentasulphide by this direct method. A preliminary experiment showed that if strong ammonia solution were treated with hydrogen sulphide in the presence of excess of sulphur, the product, as it cooled, solidified completely, thereby defeating the purpose proposed. Accordingly strong ammonia solution was diluted with an equal volume of water, excess of finely-divided sulphur added, and washed hydrogen sulphide passed in; the sulphur dissolved rapidly and a deep red liquid was obtained. When the temperature of the solution fell and the hydrogen sulphide passed through without being absorbed, it was poured into a flask and allowed to stand overnight; some crystals of anhydrous diammonium pentasulphide were deposited, but the quantity was not large. Analysis of the mother liquor showed that the ratio $NH_4 : S$ was below that required for diammonium pentasulphide, being that required for a substance of the composition $(NH_4)_4S_9$.

Repeated experiments showed that in the solution the product was invariably $(NH_4)_4S_9$; and although crystals of anhydrous diammonium pentasulphide, $(NH_4)_2S_5$, could be obtained from it with ease, a solution of diammonium pentasulphide could not be prepared. This definitely showed that a solution of diammonium pentasulphide could not be obtained either by directly dissolving sulphur in a reputed solution of diammonium monosulphide or by treating a tolerably concentrated ammonia solution simultaneously with hydrogen sulphide and sulphur, the product in solution being identical in both cases, namely tetrammonium enneasulphide, $(NH_4)_4S_9$.

Diammonium Tetrasulphide.

Attention was now devoted to obtaining crystalline diammonium tetrasulphide, $(NH_4)_2S_4$. This substance has been studied by Fritzsche (*J. pr. Chem.*, 1844, **32**, 313). After describing the method of procedure and some properties of the salt, he states that, on account of its instability, it is difficult to weigh the substance accurately for analysis, and for this reason concordant analytical results cannot be expected.

In order to test Fritzsche's method of preparing diammonium tetrasulphide, the following experiment was performed, following his directions as closely as possible. The mother liquor which had deposited crystals of diammonium pentasulphide (and containing a compound of the composition $(NH_4)_4S_9$) was cooled by ice, and treated alternately with ammonia and hydrogen sulphide, when an almost solid crystalline yellow magma was obtained, as observed by Fritzsche. Gently heating this on the water bath, the crystals dissolved, and a considerable amount of gas was evolved. On cooling, fern-like crystals were deposited, which, after the mother liquor had been poured off, were analysed. The ammonia values obtained (23·08 and 23·69 per cent. NH_4) were not constant, and were too high for diammonium tetrasulphide, which would only contain 22 per cent. NH_4. The crystals were redissolved in a little water at 40°, and the solution allowed to cool; the crystals which were deposited were analysed with the following results:—S = 72·00; 74·65 per cent. NH_4 = 17·94; 18·03 per cent. The substance is evidently not a definite compound, since a variation of 2·6 per cent. is observed in the two determinations of sulphur. The percentage of ammonium has fallen, and does not correspond with that of any definite salt. The mother liquor from the first crop of crystals was now treated in the same fashion alternately with ammonia and hydrogen sulphide, to give the method every chance of yielding tetrasulphide. A yellowish, feathery, crystalline mass was obtained, which was separated from the mother liquor, pressed, &c., and analysed. It gave S = 57·52 and 56·56. NH_4 = 33·38 and 33·63 per cent.

The solution of the crystals was only faintly yellow, and the treatment with acid showed that it contained but a very small amount of polysulphide sulphur. Apparently a high multiple grouping, $(NH_4)_2S.xNH_4{\cdot}HS$, had crystallised out, the trace of polysulphide observed being due to adherent mother liquor which it is difficult to remove, owing to the nature of the crystals.

It seems probable that the result of passing ammonia and hydrogen sulphide alternately through the polysulphide solution, $(NH_4)_4S_9$, is that this polysulphide is precipitated together with compounds of the form $(NH_4)_2,SxNH_4{\cdot}HS$.

Fritzsche's process was therefore modified. The polysulphide solution was treated alternately with ammonia and hydrogen sulphide as before, but when the semi-solid mass of crystals had formed, the mother liquor was carefully poured off, and they were dissolved in a small quantity of water at 40—50°. On cooling, yellow needles were deposited, which, when recrystallised from a small quantity of water, gave crystals of anhydrous diammonium pentasulphide. The mother liquor from these yellow needles, when cooled in a freezing mixture, deposited a yellow crystalline mass, the mother liquor was poured off, and the crystals dissolved in their water of crystallisation by warming to 20—30°. The fine yellow crystals deposited on cooling were analysed, and gave NH_4 = 21·62 and 21·67 per cent. Total, S = 76·00 and 76·10 per cent. S (polysulphide) = 56·79 per cent.

These figures show that the crystals are those of hydrated diammonium tetrasulphide, having this composition, $(NH_4)_2S_4,\frac{1}{4}H_2O$ or $4\{(NH_4)_2S_4\},H_2O$.

	Calculated for $(NH_4)_2S_4 + \frac{1}{4}H_2O$.	Found.	
NH_4................	21·36 per cent.	21·63	21·67 per cent.
Total sulphur	75·96 „	76·00	76·10 „
Polysulphide sulphur	56·97 „	56·79 „	

It is thus shown that, on treating a solution of tetrammonium enneasulphide, $(NH_4)_4S_9$, alternately with ammonia and hydrogen sulphide, a yellow crystalline magma is obtained, which, by a modification of Fritzsche's method, can be separated into diammonium pentasulphide, $(NH_4)_2S_5$, and diammonium tetrasulphide, $(NH_4)_2S_4$. The following explanation of the mode of separation is offered.

1. Alternate treatment of solution of tetrammonium enneasulphide with ammonia and hydrogen sulphide determines the precipitation of practically the whole of the polysulphide as a yellow crystalline mass composed of $(NH_4)_4S_9$ and compounds of the type $(NH_4)_2S,xNH_4{\cdot}HS$.

2. On treating this mixture with a small quantity of water at 40—50°, $(NH_4)_4S_9$ dissolves without deposition of sulphur, owing to the presence of the compounds $(NH_4)_2S,xNH_4{\cdot}HS$. On cooling, yellow needles are deposited, $[((NH_4)_2S_5,(NH_4)_2S,xNH_4{\cdot}HS\ ?)]$, which yield pure anhydrous diammonium pentasulphide on recrystallisation.

3. The mother liquor from these yellow needles deposited diammonium tetrasulphide on cooling, and in this way hydrated diammonium tetrasulphide can be obtained in a state of purity.

A consideration of Fritzsche's method for preparing the tetrasulphide renders it evident that he believed the solution, from which crystals of anhydrous diammonium pentasulphide had been deposited, still contained that substance, and he relied on the power of ammonia and hydrogen sulphide to effect a reduction of the pentasulphide to tetrasulphide. In order to determine whether such reduction took place, crystals of diammonium pentasulphide were dissolved in strong ammonia solution, and treated with hydrogen sulphide; but no reduction to diammonium tetrasulphide was observed, crystalline masses of the pentasulphide and $(NH_4)_2S,xNH_4{\cdot}HS$ groups being obtained. Fritzsche's description of the properties of his diammonium tetrasulphide is not in agreement with the behaviour of the pure salt, which is at once dissociated by water, with deposition of sulphur. Fritzsche states (*J. pr. Chem.*, 1844, **32**, 313) that "tetrasulphide of ammonium is easily soluble in water, and a concentrated solution can be kept without decomposition if well-boiled water has been used for its solution."

Fritzsche's remarks are explained by the fact that the product obtained is not pure tetrasulphide, but contains $(NH_4)_2S,xNH_4{\cdot}HS$ groups. The presence of these prevents precipitation of sulphur from the tetrasulphide in a strong solution, and retards its precipitation if the solution be diluted.

Diammonium Trisulphide.

Fritzsche (*loc. cit.*) attempted to prepare the trisulphide by the continued action of ammonia and hydrogen sulphide on the mother liquor from which his reputed tetrasulphide was obtained. He says, "In this endeavour I have not been successful. Although I obtained some colourless crystals in large laminæ, they proved on examination to be anhydrous hydrosulphide of ammonium (which therefore can be produced in the wet way)."

Fritzsche does not give details of the experiments by which he convinced himself that these crystals were ammonium hydrosulphide; the author's experiments proved, however, that the final product obtained on treating polysulphide solutions (which had yielded crystals of diammonium pentasulphide and diammonium tetrasulphide) alternately with ammonia and hydrogen sulphide was not ammonium hydrosulphide. The analysis of this final product—namely, NH_4 = 33 81 and 33·79 per cent.; S = 56 68 and 56·73 per cent.—corresponds approximately with that required by the formula $(NH_4)_2S,24NH_4{\cdot}HS$. The small amount of polysulphide mother liquor which the crystals retain after pressing between filter-paper prevents an accurate determination of their composition.

Attempts previously made (*vide* p. 298) to prepare diammonium trisulphide, $(NH_4)_2S_3$, by the action of reputed solution of $(NH_4)_2S$ on the calculated amount of sulphur in a sealed tube resulted in the production of hydrated diammonium pentasulphide, $(NH_4)_2S_5,H_2O$.

Fritzsche (*J. pr. Chem.*, 1841, **24**, 460) states that ammonium pentasulphide, when treated with water, gives a lemon-coloured solution of a compound containing less sulphur. *Watt's Dictionary* (Morley and Muir, 1, 204) states that $(NH_4)_2S_5$ occurs as orange-red prismatic crystals, easily soluble in water and alcohol (although the study of ammonium sulphides is attributed to Fritzsche). Experiments showed that both diammonium pentasulphide and diammonium tetrasulphide are decomposed by water, depositing sulphur and yielding yellow solutions. It was therefore considered possible that solutions of diammonium trisulphide and disulphide might be obtained by the decomposition of the higher polysulphides by water. The experiment was accordingly made, diammonium pentasulphide being selected on account of the ease with which it is obtained in a state of purity (p. 295). The crystals were rapidly transferred to a wide-mouthed, stoppered bottle, and cold, recently-boiled water added until no further precipitation of sulphur followed the addition of a small quantity of water. The clear, bright golden-yellow solution thus obtained must contain either a mixture of polysulphides lower than tetrasulphide (trisulphide and disulphide) or one of them.

From the results of the analysis—namely, NH_4 = 0 69, 0·68, and 0·68 per cent.; total S = 2·05 per cent.; polysulphide S = 1·37 per cent.—it is concluded that the solution is one of diammonium trisulphide $(NH_4)_2S_3$, the ratio of the polysulphide sulphur to that as $(NH_4)_2S$ being as 2 : 1.

Total sulphur found	2·05	per cent.
Sulphur as polysulphide	1·37	”
Sulphur as $(NH_4)_2S$	0·68	”

Diammonium Disulphide

The statement that "An aqueous solution may be prepared by dissolving S in $(NH_4)_2S$,Aq in the proportion $(NH_4)_2S$: S" (*Watt's Dictionary*, Morley and Muir, 1, 204) has been proved to be erroneous (see p. 298), the polysulphide obtained under these conditions being hydrated tetrammonium heptasulphide, $(NH_4)_4S_7,4H_2O$.

A second method (*Watt's Dict*, Morley and Muir, *loc. cit.*) consists in passing the vapour of sulphur and of ammonium chloride through a hot porcelain tube and then into a well-cooled receiver. On making the experiment, however, it was found that the product consisted merely of ammonium chloride and sulphur.

No authority is given for these methods, and in the latter case, having regard to the instability of the ammonium sulphides when subjected to the action of heat, the probability of obtaining a definite polysulphide by condensation, after passage through a hot tube, is somewhat remote. Up to the present, diammonium disulphide has not been obtained either in crystals or in solution.

Diammonium Enneasulphide.

In the course of these experiments, a solution of tetrammonium enneasulphide, $(NH_4)_4S_9$, had been prepared by diluting 500 c.c. of strong ammonia solution with 150 c.c. of water, and treating simultaneously with hydrogen sulphide and excess of sulphur. The deep red solution deposited crystals of anhydrous diammonium pentasulphide on standing; as these crystals were required for experiments, the red mother liquor was poured off into a large flask, which was provided with a loosely-fitting cork. After some months, it was observed that a large quantity of small, hard, shining crystals of a deep red colour had been deposited; their form is difficult to distinguish, as they occur in closely-aggregated, crystalline masses. The experimental conditions were similar to those under which Fritzsche claims to have obtained diammonium heptasulphide, and for which search had been made by the author without success up to this time.

The main bulk of mother liquor was poured off into flasks loosely fitted with corks, leaving sufficient, however, to protect the crystals. Some of the crystals were pressed between filter-paper, and analysed with the following results. $NH_4 = 10{\cdot}81$ per cent. Total $S = 86{\cdot}47$ and $86{\cdot}55$ per cent. Polysulphide $S = 77{\cdot}05$ per cent. The crystals were not, as expected, those of diammonium heptasulphide, but were richer in sulphur, and of the composition $(NH_4)_2S_9,\frac{1}{2}H_2O$, hydrated diammonium enneasulphide, which would require

	Total S.	NH_4.	H_2O.	Polysulphide S.
Calculated for $(NH_4)_2S_9\frac{1}{2}H_2O$	86·49	10·81	2·70	76·88 per cent.
Found....................	86·51	10·81	(2·68)	77·05 ,,

The mother liquor from these crystals, preserved in loosely-corked flasks, deposited another crop of crystals which, on analysis, proved to be diammonium enneasulphide, containing more water of crystallisation, $5(NH_4)_2S_9 + 4H_2O$.

This compound is remarkable as being the highest sulphide obtained; the crystals when covered with mother liquor appear almost black, but on removal from the mother liquor are seen to be of a deep ruby colour and almost opaque. If rapidly freed from mother liquor only a thin film of sulphur is formed on the crystals. If the crystals are treated with water they are decomposed, and dissolve to a limited extent, yielding a pale yellow solution of a lower sulphide, whilst a sulphur-coated crystal is left preserving the form of the original.

The behaviour of this salt with acids is characteristic; the exterior of the crystal becomes coated with a hard mass of sulphur, which protects it against the action of dilute hydrochloric acid, even when boiled with it. In estimating the ammonium and sulphur (polysulphide), it was necessary to break down the sulphur-coated crystals with a flat-ended glass rod, the crystals being hard and vitreous, boiling with acid and repetition of the process of crushing being continued until the decomposition was complete.

The crystals of diammonium enneasulphide, if pressed with a glass rod against a hard surface, fly to pieces, the powder having the colour of finely-divided potassium dichromate.

Diammonium Heptasulphide.

Throughout these experiments, no crystals of diammonium heptasulphide had been obtained, although the pentasulphide and enneasulphide were prepared in a state of purity.

Fritzsche states (*J. pr. Chem.*, 1841, **24**, 460) that diammonium heptasulphide is formed from the pentasulphide while it is being drained from mother liquor; the crystals were placed in a bottle, which stood with the cork downwards in order to allow the mother liquor to drain off, air being excluded.

"After some days, many of the crystals of the pentasulphide carried new, small, ruby-coloured crystals, and others bore cavities sideways which were filled up with the new substance; that, however, only adhered loosely to the crystal out of which it had been formed. The decomposition becomes complete on standing for a longer time, especially when the vessel is large and filled with dry air. The new compound appears then in the form of a crystalline crust, resembling in shape the original crystal, but larger and hollow in the centre."

I found, however, that on limited exposure to air of the liquid resulting from solution of crystals of diammonium pentasulphide in their own mother liquor, crystals of sulphur are deposited, together with diammonium pentasulphide, but no red crystals such as Fritzsche described.

Diammonium heptasulphide has, however, been obtained by the simultaneous action of hydrogen sulphide and sulphur on solutions of ammonia; the ammonia solutions being more concentrated than those used in preparation of diammonium pentasulphide. For instance, 200 c.c. of strong ammonia solution (0·880) were diluted with 60 c.c. of water, excess of sulphur added, and hydrogen sulphide passed to saturation, the flask and contents being kept in constant agitation to promote solution. When the hydrogen sulphide passed through the solution without being absorbed, and the temperature of the solution began to fall, the latter was carefully poured off from the undissolved sulphur into another flask. Small glistening, red crystals at once began to form, and continued to increase even when the flask was placed in warm water.

On analysis, they gave the following results: NH_4 = 12·80 and 12·65 per cent. Total S = 78·96 per cent. Polysulphide S = 66·81 per cent.

These figures correspond to hydrated diammonium heptasulphide, $3(NH_4)_2S_7,4H_2O$, for which the following values would be required.

	NH_4.	Total S.	Polysulphide S.
Calculated for $3(NH_4)_2S_7,4H_2O$	12·67	78·87	67·60 per cent.
Found	12·65	78·96	66·81 „

The crystals when dry appeared dichroic, exhibiting a peculiar violet lustre. Examined with a lens they seemed to be tetrahedra. They maintained their form in air, becoming, however, slowly coated with sulphur. In contact with water, the crystals underwent decomposition, depositing sulphur, and yielding a pale yellow solution. They were only slowly attacked by dilute hydrochloric acid, but did not resist the action of acid so strongly as the crystals of diammonium enneasulphide.

Remarks on the Formation of Polysulphides.

The mode of formation of the polysulphides of ammonium does not seem to be as simple as is usually considered. The statement is made that in the case of diammonium disulphide, $(NH_4)_2S_2$, an aqueous solution may be prepared by dissolving S in $(NH_4)_2S,Aq$ in the required proportion, thus

$$(NH_4)_2S + S = (NH_4)_2S_2.$$

On heating a solution, corresponding to $(NH_4)_2S$, in sealed tubes with the calculated amounts of sulphur, the desired polysulphides were not obtained (see p. 297).

$$(NH_4)_2S + S \text{ gave } (NH_4)_4S_7,4H_2O.$$
$$(NH_4)_2S + S_2 \text{ ,, } (NH_4)_2S_5,H_2O.$$
$$(NH_4)_2S + S_3 \text{ ,, } (NH_4)_4S_9,3\tfrac{1}{2}H_2O.$$

It was proved that more sulphur than is represented by the last equation could not be dissolved.

On warming a moderately strong solution of $(NH_4)_2S$ with excess of sulphur in an open vessel, until no more of the latter is dissolved, allowing to cool, pouring off the deep red solution from the excess of sulphur, and cooling in a freezing mixture, a yellow crystalline mass is deposited; this, on gently warming, dissolves in its own water of crystallisation, forming a deep red liquid. The composition of this solution is represented by the formula $(NH_4)_4S_9$, tetrammonium enneasulphide, and in several different experiments the same compound was always produced.

It was thought possible that the fact that the simple polysulphides were not formed, was due to the constitution of the reputed solution of $(NH_4)_2S$, which, as has been shown, has not this formula, but must be regarded as a solution of $(NH_4)_2S,2NH_4{\cdot}HS + 2NH_4{\cdot}HO$.

In the hope of obtaining the simple polysulphides by the action of sulphur on $(NH_4)_2S$ at the moment of its formation, another method of preparation was attempted. Hydrogen sulphide was passed into a solution of ammonia, of a strength corresponding to the solution of $(NH_4)_2S,2NH_4{\cdot}HS + 2NH_4{\cdot}HO$ previously used, in the presence of sulphur, as already described. The solution obtained, however, had also the composition $(NH_4)_4S_9$, and was proved to be free from ammonium hydroxide or hydrosulphide by means of the cupric sulphate test. It was also free from oxidised sulphur.

It would seem then that whichever method of preparation was adopted the polysulphides obtained contain four ammonium groups. Thus the solution containing $(NH_4)_2S,2NH_4{\cdot}HS + 2NH_4{\cdot}HO$ will dissolve sulphur in the cold with evolution of some hydrogen sulphide, and if it be agitated when no more sulphur is dissolved tetrammonium heptasulphide, $(NH_4)_4S_7$, crystallises out.

On warming solutions containing $(NH_4)_2S,2NH_4{\cdot}HS + 2NH_4{\cdot}HO$ with excess of sulphur, the chief product obtained is tetrammonium enneasulphide, $(NH_4)_4S_9$.

No experimental evidence could be obtained of the direct formation of the simple or diammonium polysulphides.

It appears that when a solution containing $(NH_4)_2S,2NH_4{\cdot}HS + 2NH_4{\cdot}HO$ acts on sulphur, the compound $(NH_4)_2S,2NH_4{\cdot}HS$ loses hydrogen sulphide, and, according to the conditions of experiment, takes up 5 or 7 atoms of sulphur.

$$(a.)\ (NH_4)_2S,2NH_4\cdot HS + S_5 = (NH_4)_4S_2\cdot S_5 + H_2S.$$
$$(b.)\ (NH_4)_2S,2NH_4\cdot HS + S_7 = (NH_4)_4S_2\cdot S_7 + H_2S.$$

The saturated red liquor obtained by the action of a solution of $(NH_4)_2S,2NH_4\cdot HS$ on sulphur cannot be induced to take up more sulphur than enough to form tetrammonium enneasulphide $(NH_4)_4S_9$, and it would appear that all the simple or diammonium polysulphides obtained are secondary products, formed by the decomposition of tetrammonium enneasulphide under varying conditions of temperature, concentration, &c.

Thus, when the original saturated red solutions of the enneasulphide are of suitable strengths, the following simple or diammonium polysulphides can be obtained.

$(NH_4)_2S_5$ = diammonium pentasulphide.
$(NH_4)_2S_7$ = ,, heptasulphide.
$(NH_4)_2S_9$ = ,, enneasulphide.

But in all cases the mother liquors left after separation of the crystals have a lower sulphur value than is required by $(NH_4)_4S_9$. Also by alternately treating a solution of the enneasulphide with ammonia and hydrogen sulphide, and by slightly modifying Fritzsche's process (see p. 302), it has been found possible to resolve tetrammonium enneasulphide, $(NH_4)_4S_9$, into diammonium pentasulphide, $(NH_4)_2S_5$, and diammonium tetrasulphide, $(NH_4)_2S_4$, both these substances being obtained pure.

The study of the exact conditions under which tetrammonium enneasulphide will yield the diammonium polysulphides is greatly complicated by the circumstance that it is decomposed by water, and up to the present no vehicle has been found available for its recrystallisation.

The author wishes to express his acknowledgment of the services rendered by his assistant, Dr. W. J. McKerrow, who has in the course of this work displayed much resource in meeting the many difficulties encountered.

XXXVI.—*Note on the Action, in the Cold, of Diastase on Starch-paste.*

By HORACE T. BROWN, F.R.S., and G. HARRIS MORRIS, Ph.D., F.I.C.

AMONGST the fundamental facts which must be taken into account in any serious attempt to explain the changes which occur during the transformation of starch by diastase, there is none of more importance than the well-marked relation which always exists between the opticity and the cupric reducing power of the products of the hydrolysis. Given the cupric reducing power of the mixed conversion products at any stage of the transformation between soluble starch and maltose, it is possible, with a remarkable degree of accuracy, to predict the polarimeter reading, and consequently the specific rotatory power of the matter in solution; whilst, on the other hand, if the specific rotatory power of the starch products has been determined, the cupric reduction can be deduced from this with equal accuracy. This important generalisation, which naturally follows from the early work of O'Sullivan on the end-products of the action, was proved to be correct by the work of one of us in conjunction with Heron (Trans., 1879, **33**, 596—655), and was further confirmed and strongly insisted upon in our paper on the "Non-crystallisable Products of the Action of Diastase on Starch," published in 1885 (Trans., 1885, **47**, 527—570). In the last-mentioned paper, we showed that the striking relation between opticity and cupric reducing power holds good not only for the mixed products of transformation at any stage of the reaction, but also for any fractionally separated portions of the products, no matter whether this separation has been brought about by fractional treatment with alcohol, by dialysis, or by any other means. In all these cases, the whole or any fractional part of the products can always be expressed, quite consistently with the opticity and cupric reducing power, in terms of *maltose* having a specific rotatory power of $(\alpha)_{j3\cdot86}150°$. and a reducing power of $\kappa_{3\cdot86}61$; and of a non-reducing dextrin of $(\alpha)_{j3\cdot86}216°$. This is quite independent of any consideration as to the true nature of the intermediate products between starch and maltose, and may, for our present purposes, be regarded as merely an empirical generalisation, based on such a large amount of experimental evidence as to admit of no doubt.

Strange to say, this constant and consistent relation of opticity and cupric reducing power has been altogether ignored by recent workers on starch hydrolysis, and we are, in consequence, frequently asked to accept as homogeneous substances and chemical entities, fractionated products having opticities and cupric reducing powers hopelessly at variance with each other.

We shall have occasion, at no distant date, of enlarging on this point in a re-examination of the whole question of starch hydrolysis by diastase; our only reason for commenting on it at the present time is to call attention to an apparent exception to this rule of consistent opticity and cupric reduction, which first came under our notice 16 years ago, and of which, at that time, an erroneous explanation was given.

In the 1879 paper above mentioned (Brown and Heron, *loc. cit.*) it was noted that when starch transformations are brought about by the action of diastase (cold water malt-extract) at *ordinary temperatures*, the optical activity of the mixed products is lower than it ought to be from a consideration of the cupric reducing power, if the above generalisation is to be accepted. Thus, in one experiment in which 3·7 grams of starch, in the form of starch-paste, had been acted on by 10 c.c. of normal malt-extract for 60 minutes, the following results were obtained for the final products.

$(\alpha)_{j3\cdot86}$ 157·5° $\kappa_{3\cdot86}$ 44·1.

Now this reducing power indicates the presence of 100 × 44·1 ÷ 61 = 72·3 per cent. of maltose in the mixed products, and if the remainder is dextrin, the mixture ought to have an opticity of $(\alpha)_{j3\cdot86}$ 168·4°, instead of the 157·5° actually observed. On standing for three hours longer, both the *opticity* and the reducing power were found to *rise*, the specific rotatory power and cupric reduction being then as follows.

$(\alpha)_{j3\cdot86}$ 161·6° $\kappa_{3\cdot86}$ 49·7.

The reducing power now corresponds to 81·5 per cent. of maltose, and if the balance of 18·5 per cent. is supposed to be dextrin, the calculated opticity becomes 162·2° against 161·6° actually observed.

This phenomenon is always observed in transformations of starch-paste in the cold, that is, the observed angle is at first too low for the reducing power, but becomes consistent with it if left for some time. This was explained at the time as probably arising from the dissolution and gradual hydrolysis of a small quantity of starch-cellulose, but the explanation was never deemed satisfactory or sufficient.

At the time these observations were published, the so-called "half rotation" of maltose had not been recognised. It is true that the birotation (as distinct from the half rotation) of certain of the carbohydrates had already been observed, but it had been expressly stated by certain observers that maltose did not possess this property.

The term "half rotation" was first used by Schmöger to express the fact that the optical activity of one variety of milk sugar was found to be less in a freshly-made solution than in one which had stood for some hours, or had been boiled. Shortly afterwards the same observation with regard to maltose was made by Meissl and others, and the difference between the specific rotation in freshly-prepared solutions, and in solutions which had stood for some time, was given as from 15° to 20°.

The following are the details of the specific rotation of pure, crystallised maltose, which we ourselves have observed under these circumstances.

	Solutions freshly prepared.	Solutions after boiling.
$(a)_{j3\cdot83}$	133·5°	150·2°,

showing a difference of 16·7°.

It was shown by C. O'Sullivan and Tompson in 1890 (Trans., 1890, **57**, 920), that when cane sugar in aqueous solution is inverted by invertase in the cold, the dextrose at the moment of hydrolysis is liberated in the birotatory state. It was also found that the birotation, both in this case and in the case of a freshly-prepared solution of the crystalline sugar, is instantly destroyed by the addition of a small amount of potassium hydrate. Later, Schulze and Tollens (*Annalen*, 1892, **271**, 49) furnished experimental proof that the same effect is produced by the addition of 0·1 per cent. of ammonium hydrate.

The observations of O'Sullivan and Tompson suggested to us the possibility that the abnormal results observed on hydrolysing starch-paste in the cold were due to the liberation of the maltose in the "half rotatory" state, and the probability of this was rendered still greater by the fact that these abnormal starch conversions rapidly become normal on standing or on heating, and also by the fact that, when at their maximum divergence from the rule stated above, the results may be regarded as indicating the existence, besides the dextrin, of a substance having an opticity of $(a)_{j3\cdot86}$ 135·1°, approximately that of "half rotatory" maltose.

In order to place this conclusion beyond doubt, some comparative experiments were made with starch conversions in the cold, both with and without the addition of alkali.

Ammonium hydrate was chosen as being the most convenient alkali to use, and its action was in the first place tried on a freshly-prepared *cold* solution of crystallised maltose. A 5 per cent. solution of the maltose having been prepared, its optical activity was at once determined. The solution was then divided into two parts; to one 0·1 per cent. of ammonia was added, the other was boiled for a few moments. The following results were obtained.

	Specific rotation.
Freshly-prepared solution	133·5°
Solution after addition of ammonia	150·3
,, ,, boiling	150·3

The "half rotation" of the maltose in the freshly-prepared solution had been, therefore, instantly destroyed by 0·1 per cent. of ammonia, as also by boiling the solution.

A 4 per cent. starch-paste was then prepared, and, when cold, was hydrolysed with cold water malt-extract at the rate of 8·33 c.c. per 100 c.c. At the end of 30 minutes, the solution, which had undergone conversion, was divided into two parts. To one of these, A, was added salicylic acid in the proportion of 0·05 gram per 100 c.c., in order to stop the action of the diastase, and thus to stereotype the starch products until a rapid analysis could be made; whilst to the other portion, B, 0·1 per cent. of ammonia was added. The results were—

	A.	B.
$[\alpha]_{j3\cdot 56}$	156·4°	167·9°
$\kappa_{3\cdot 56}$	45·03	44·39

In A, the angle calculated from the reducing power, on the assumption that dextrin and ordinary maltose alone are present, should be 167·2° instead of 156·4° the angle actually observed; whilst the addition of the ammonia had suddenly brought up the angle, and the conversion is quite a normal and consistent one, the angle calculated from the reducing power being 167·97° against 167·9° actually observed.

If in A we take the value of the rotatory power of maltose at 135·3°, that is, approximately the specific rotatory power of "half rotation" maltose, the angle of the mixed products of transformation, calculated from the reducing power, agrees exactly with the observed angle.

A further experiment was made, under identical conditions to the last, but using soluble starch, prepared by the action of dilute hydrochloric acid on starch granules in the cold, instead of starch-paste. The results agreed closely with the foregoing, and were as follows: A being the conversion stopped with salicylic acid, and B that to which was added 0·1 per cent. of ammonia.

	A.	B.
$[\alpha]_{j3\cdot 86}$	153·9°	165·8°
$\kappa_{3\cdot 86}$	45·52	46·6

When the values in A are calculated out in the manner previously described, they require the maltose to have a specific rotatory power of 132·8°, a number which closely approximates to the angle of "half rotation," whilst B gives numbers which are theoretically correct, and absolutely consistent with the presence of maltose and dextrin only, having the values given above.

We consider that these experiments conclusively prove that in starch transformations made with diastase in the cold, the maltose is liberated in the "half rotatory" state, and that the apparent temporary departure from the ordinary rule of starch hydrolysis, namely, that the specific rotation must always bear a certain constant relation to the cupric reducing power, is due entirely to this fact. We have no doubt that the same fact explains the discrepancy in the results obtained by the action of malt-extract on bruised starch granules in the cold; a discrepancy which was commented on in the paper previously mentioned.

XXXVII.—*Titration of Iodine Solutions with Barium Thiosulphate.*

By R. T. Plimpton, Ph.D., and J. C. Chorley.

Some years ago, we were led to examine the properties of barium thiosulphate with a view of finding a substance which could easily be obtained pure, and suitable for the purpose of standardising iodine solutions. We found that barium thiosulphate possessed many advantages over sodium thiosulphate, arsenious oxide and other substances in this respect, and, after considerable experience of its use, can recommend it with some confidence.

The salt, which is only slightly soluble in cold water, reacts readily with iodine, and, as the product of its oxidation, namely the tetrathionate, is soluble, the progress of the action is marked by the gradual disappearance of the suspended crystals. The high molecular weight of barium thiosulphate, BaS_2O_3,H_2O—267 parts corresponding to 127 parts of iodine—is another advantage, and it leaves nothing to be desired with regard to the ease with which it can be prepared pure, or to its stability.

In our early experiments, the results obtained were very irregular, and we accordingly carefully examined the salt for various impurities without however being able to detect any. It was afterwards found that the error lay in drying the substance at 100°, at which temperature part of its water is lost. Pape states that the salt gives off its water at 215°, and Rose, that it retains its water of crystallisation with great tenacity; but Letts (this Journal, 1870, 23, 424) found that all the water is expelled at 100°. Not being aware of Letts' statement at the time, we made fresh experiments on the behaviour of the salt in this respect.

2·515 grams dried for five hours at 56—58° lost only 1 milligram, but at 68—70° there was a loss of 0·018 in the same time, and after long drying at this temperature, 88 per cent. of the water was expelled; the salt was eventually obtained anhydrous at 120°, 0·169 gram being lost instead of 0·1695, calculated.

Preparation.—40 grams of barium chloride dissolved in 300 c.c. of water is poured into a solution of 50 grams of sodium thiosulphate in the same quantity of water, both solutions being warm; the fine crystalline powder which separates on stirring is collected, thoroughly washed with cold water, partially dried on a porous plate, and finally at a temperature of 25—30°. It is better not to employ a pump, or to compress the powder in any way which would cause it to cake. The dry powder when properly prepared forms no lumps on shaking with water, and is then quickly acted on by iodine. Using the above quantities, about 37 grams of thiosulphate is obtained.

Titration.—A convenient quantity of the thiosulphate is weighed and placed with some water in a stoppered bottle. The iodine solution is then gradually run in, with constant shaking, until only a small quantity of thiosulphate remains. Starch is then added and the titration completed, care being taken to make sure that the blue colour remains after vigorous shaking. BaS_2O_3,H_2O (267) = I (127).

We have found the results obtained by this method uniformly satisfactory, and the thiosulphate may be kept for an indefinite time without apparent change. On examination, a specimen which had been prepared about three months before showed no sign of alteration.

Wishing on one occasion to have independent testimony as to results to be obtained with barium thiosulphate, we sent some of the substance to Mr. A. C. Chapman, who was kind enough to make the following determinations with a specially prepared solution of pure iodine.

1. Iodine indicated......	0·0951 gram.	Taken	0·0955.
2. ,, ,, ...	0 2378 ,,	,,	0·2380.
3. ,, ,, ...	0·2854 ,,	,,	0·2855.

XXXVIII.—*On Latent Heat of Fusion.*

By Holland Crompton.

It is with the object of contributing to our knowledge of the relationship between latent heat of fusion and chemical constitution that the results recorded in the present paper are brought forward. Although incomplete in themselves, and at present purely of an empirical character, it is hoped that they may at least serve to encourage further investigation, and to indicate the direction in which more definite results may be expected.

Attention has been primarily given to the entropy change attending the passage of the molecule—or, in the case of elements, of the atom—from the solid to the liquid state. A measure of this quantity is obtained by dividing the molecular—or atomic—latent heat of fusion by the absolute temperature of fusion. Throughout this paper, the symbol w is taken to indicate the latent heat of fusion of unit weight of substance; ρ is this number multiplied by the molecular—or atomic—weight, the quantity that is called the molecular latent heat of fusion; and T is the absolute temperature of fusion. The entropy change above alluded to is given, therefore, by the quantity ρ/T.

In the case of the metallic elements, an examination of the values of ρ/T shows that these are approximately proportional to the valencies of the elements, or, in other words, if these values are divided by the valencies, a constant is obtained. There is, therefore, a practically constant entropy change in the passage of equivalent quantities of the metallic elements from the solid to the liquid condition. The numbers given in Table I, the fifth column of which gives the valencies, v, and the sixth the values of the constant $C = \rho/Tv$, illustrate this point.

TABLE I.

Metal.	w.	T.	ρ	v.	C.
Mercury	2·82	234	565	2	1·207
Gallium	19·11	286	1336	3	1·557
Tin	13·32	503	1573	2	1·563
Cadmium	13·66	593	1531	2	1·291
Bismuth	12·51	540	2602	3	1·605
Lead	5·62	598	1163	2	0·972
Zinc	28·13	688	1839	2	1·336
Silver	21·07	1272	2275	1	1·789
Palladium	36·30	1773	3873	2	1·092
Platinum	27·18	2052	5295	2	1·290
				Mean	= 1·370

The table contains all the metals the latent heats of fusion of which are at present known with any degree of certainty. Taking into consideration the somewhat large margin for possible error that must be allowed in the values of both w and T in these cases, the agreement between the numbers in the sixth column is satisfactory. Where the valency of the metal varies, as for instance with tin, bismuth, and lead, the valency in the lower compounds, in which the electro-positive character of the element is most pronounced, has been taken. This selection is in keeping with the general results of this paper.

A consideration of the non-metallic elements shows that the law which has been enunciated for the metals cannot be directly extended to these. The latent heats of fusion are only known for four of the non-metals—bromine, iodine, phosphorus, and sulphur. Bromine and iodine, to be in any sense in keeping with the metals, would have to be considered as acting with triad valency, an assumption that is perhaps not so completely unjustifiable as would at first sight appear, when it is remembered that the valency with which the atoms of the free element combine with one another is quite unknown, and that in the existence of the compound ICl_3 we have presumptive evidence that one halogen may behave with triad valency towards another. It will also be shown later on that, in their compounds generally, it is necessary to assume a triad valency for the halogens as far as the latent heat of fusion is concerned, in order to bring the behaviour of these compounds into harmony with that of other substances. Phosphorus and sulphur exhibit a behaviour which is entirely different, and one that is in all probability characteristic of the non-metals, with the exception of the halogens and oxygen. For in the case of these two elements, the quantity ρ/T is not directly but *inversely* proportional to the valency, and, in order to obtain the constant, C, this quantity must be divided by the *reciprocal* of the valency. The values for the above-mentioned non-metallic elements, obtained in the manner indicated, are given below. In this table, v, for phosphorus and sulphur, is the reciprocal of the valency.

TABLE II.

Element.	w.	T.	ρ.	v.	C.
Bromine............	16·185	265·7	1294	3	1·623
Iodine..............	11·71	387	1485	3	1·278
Phosphorus.........	5·03	317·2	156·1	0·33	1·476
Sulphur............	9·368	388	300·3	0·5	1·548
				Mean	= 1·481

It is now possible to extend the method employed above in considering the latent heats of fusion of the elements to compound substances. In doing this, the principles to be adopted as derived from the results hitherto obtained are to consider the values of ρ/T as directly proportional to the valency in the case of metallic or electropositive elements, and as inversely proportional to the valency in the case of non-metallic or electro-negative elements. Assuming, therefore, that the regularities which apply in the case of the free elements can without any modification be directly applied to the same elements in their various compounds, we should expect that on taking the product, ρ, of the latent heat, w, and the molecular weight, M, and dividing it by the product of the absolute melting point, T, and the sum of the valencies or their reciprocals of the different atoms in the molecule of the compound—a quantity to which the symbol Σv may be given—the constant C would be obtained.

It is, however, obviously improbable that a rule which holds in the case of the free elements should be capable of immediate extension, without any modification, to compounds. This is further shown when the numbers obtained by the method indicated are examined, the discrepancies among the numbers themselves, and the wide divergencies from the mean values previously obtained for C, proving at once that some modification of the general law is necessary before it can be extended to compounds.

This modification appears to be contained in the assumption, that whenever an electro-positive element is directly united to an electro-negative element, the value of v for the electro-positive element must be considered as reduced by an amount which is equal to its own valency divided by that of the element to which it is united. Thus, if an electro-positive element, having the normal valency 1, were united to carbon, v would have to be considered as reduced to 0·75; when united to triad nitrogen, v would be reduced to 0·666, with pentad nitrogen to 0·8, and so on.

In addition to the above, a number of other points appear in the investigation of the behaviour of compounds.

In the first place, the value of v for hydrogen must be considered as somewhat less than unity. The number 0·75 has been chosen empirically, and is used throughout this investigation to represent the value of v for hydrogen.

Secondly, the halogens are considered throughout as having the value $v = 3$, as has been already stated when discussing the behaviour of bromine and iodine in the free state. It is also necessary to assume that the halogens and oxygen behave in their compounds like the electro-positive, and not like the rest of the electro-negative elements.

Lastly, if an element has a greater valency than unity, the active valency as affecting the latent heat of fusion must be considered as definitely modified by the mode of union with other elements. Thus oxygen, which has a full valency of two, acts with this valency only when it is directly united to two other monad atoms or radicles, or generally in compounds of the type $R'—O—R_1'$; but when both of the bonds of the oxygen atom are occupied by one and the same diad atom or radicle, as in the compound $R''=O$, the active valency of the oxygen can only be regarded as unity. In other words, in estimating the active valency of an element, it is necessary in this investigation to leave out of account what may perhaps be termed the latent bonds of union, and to consider a double or triple linking to have only the value attaching to a single one. The case of carbon offers a good illustration.

$-\overset{|}{\underset{|}{C}}-$ is considered as tetrad, and has the valency 0·25.

$=C<$ is considered as triad, and has the valency 0·33.

$\equiv C-$ and $=C=$ are considered as diad, and have the valency 0·5.

This change in the active valency of an element has, however, no effect on the influence already described, which an electro-negative element is considered as exercising over an electro-positive element, this influence being invariably inversely proportional to the full nominal valency of the electro-negative element.

As an illustration of the method of applying the above rules, a calculation of Σv in the case of sulphuric acid may here be given. Assuming that sulphuric acid has the usually accepted constitution $O_2S(OH)_2$, we have in this compound in the first place a hexad sulphur atom, two of whose bonds are latent, and the value for v of which is, therefore, that which would attach to an electro-negative tetrad atom, namely, 0·25. The sulphur is directly united to four oxygen atoms, two of whose total of eight bonds are latent. The full value of v for the oxygen atoms would, therefore, be 6, but as oxygen acts as an electro-positive element, and is here attached to a hexad electro-negative element, this value must be reduced by $\frac{1}{6} \times 6$, and the final value is, therefore, 5. The two hydrogen atoms have a value for v of 1·5, which requires no further modification, as here electro-positive hydrogen is united directly to electro-positive oxygen. Summing the values thus obtained for sulphur, oxygen, and hydrogen, we finally have for sulphuric acid $\Sigma v = 6·75$.

Table III contains the values obtained for C in the case of inorganic compounds. Several of these are salts containing water of crystallisation, and in these cases, in the absence of any guiding principle, each molecule of water present has been given the value of v, which attaches to it in the free state, except in the case of the compound H_2SO_4,H_2O, for which the constitution $OS(OH)_4$ has been assumed.

TABLE III.

Compound.	w.	T.	ρ.	Σv.	C.
Water, H_2O	79·89	273·0	1439	3·5	1·506
Chloride of iodine, ICl	14·15	289·5	2297	6·0	1·322
Sulphuric acid, $O_2S(OH)_2$	24·03	283·5	2355	6·75	1·232
" monohydrate, $OS(OH)_4$	39·92	281·5	4631	10·70	1·538
Hypophosphorus acid, $OPH_2(OH)$	36·36	290·4	2400	4·60	1·797
Phosphorous acid, $OPH(OH)_2$	37·44	291·0	3070	6·35	1·661
Phosphoric acid, $OP(OH)_3$	25·71	291·0	2520	7·90	1·096
Lead chloride, $PbCl_2$	20·90	758·0	5806	8·0	0·958
Lead bromide, $PbBr_2$	12·34	763·0	4526	8·0	0·742
Lead iodide, PbI_2	11·50	648·0	5297	8·0	1·021
Potassium nitrate, $O_2N(OK)$	48·90	606·5	4949	4·53	1·801
Sodium nitrate, $O_2N(ONa)$	64·87	578·5	5520	4·53	2·105
Calcium chloride, $CaCl_26H_2O$	40·70	301·5	8909	29·0	1·019
Calcium nitrate, $CaN_2O_64H_2O$	33·49	315·4	7907	23·07	1·087
Sodium phosphate, $Na_2HPO_412H_2O$	66·80	309·4	23920	50·40	1·534
Sodium thiosulphate, $Na_2S_2O_35H_2O$	37·60	282·9	9332	24·75	1·333
Sodium chromate, $Na_2CrO_410H_2O$	37·43	296·0	12850	42·25	1·028
				Mean =	1·340

It will be seen on reference to the table that the greatest variation from the mean value of *C* is observed, more particularly in cases in which the accurate determination of either *w* or T, or of both, would be likely to present difficulty. This is the case, for example, with the

TABLE IV.

Compound.	*w*.	T.	*ρ*.	Σ*v*	*C*.
Formic acid	57·38	265·5	2640	3·89	2·556
Acetic acid	44·34	277·2	2661	5·27	1·822
Lauric acid	44·90	316·4	8985	19·02	1·494
Myristic acid	47·50	326·8	10836	21·77	1·523
Palmitic acid	39·2	328·0	10040	24·32	1·248
Stearic acid	47·6	337·0	13520	27·25	1·472
Phenylacetic acid	25·4	347·9	3454	9·52	1·013
Crotonic acid	25·3	340·4	2176	7·06	0·905
Glycerol	42·5	286·0	3911	10·31	1·327
Methylic oxalate	42·6	322·5	5027	9·05	1 722
Spermaceti	36 98	316·9	17761	46·33	1·210
Urethane	40·8	321·7	3634	7·22	1·564
Ethylene dibromide	12·91	280·9	2432	7·25	1·194
Chloral hydrate	33·22	319·0	5491	12 31	1·309
Bromal hydrate	16·9	319·0	5053	12·31	1·287
Benzene	29·9	278·4	2333	5·375	1·559
Paraxylene	39·3	289·0	4168	8·13	1·774
Paradichlorobenzene	29·9	325·5	4395	8·75	1·513
Paradibromobenzene	20·6	357·9	4802	8·75	1·552
Parabromotoluene	20·15	289·5	3446	8·44	1·410
Dichloroparaxylene	32·70	373·0	5721	11·5	1·334
Dichlorortho-xylene	29·00	328·0	5071	11·5	1·312
Dichlorometaxylene	26·70	307·0	4671	11·5	1·323
Dibromortho-xylene	21·25	368·0	6101	11·5	1·513
Dibromometaxylene	21·45	350·0	5662	11·5	1·107
Tetrachloroparaxylene	22·10	368·0	5389	11·88	0·981
Tetrachlorortho-xylene	21·00	359·0	5121	11 88	0·958
Nitrobenzene	22·30	263·8	2711	6·71	1·513
Metachloronitrobenzene	29·1	316·8	1632	8·13	1·775
Parachloronitrobenzene	21·4	355·0	3370	8·43	1·126
Paratoluidine	39·0	311·9	4177	7·52	1·781
Parachloraniline	37·2	312·0	4712	7·83	1·771
Phenol	24·93	298·4	2341	7·06	1·113
Paracresol	26·3	307·0	2810	8·11	1·096
Thymol	27·5	321·2	4127	12·56	1·023
Orthonitrophenol	26·8	315·8	3725	8·43	1·399
Naphthalene	35·60	352·7	4559	8·17	1·582
Nitronaphthalene	25·32	329·0	4383	9·54	1·396
α-Naphthylamine	22·3	320·5	3189	8·91	1·113
Diphenyl	28·5	313·2	4391	9·62	1 330
Benzophenone	23·7	321·0	4313	10·70	1·256
Diphenylamine	21·30	321·0	3602	10·45	1·061
Azobenzene	28 5	342·0	5187	10·62	1·128
Azoxybenzene	21·6	307·6	4277	10·95	1·270
Menthol	18·9	315·0	2948	?16·01	[illegible]
				Mean =	[illegible]

halogen compounds of lead and the nitrates of potassium and sodium. The extreme variation noticed in the case of lead bromide is doubtless of this origin. For it must be regarded as improbable that, on the one hand, the melting point of the bromide should be higher than that of the chloride, and at the same time so far removed from that of the iodide, and that, on the other hand, the latent heat of fusion of the bromide should be so nearly equal to that of the iodide, and so far removed from that of the chloride.

The organic compounds whose latent heats of fusion have been directly determined are considered in Table IV. The necessary data have been obtained from Landolt and Börnstein's tables, the results of Eykman (*Zeit. physikal. Chem.*, 1889, **4**, 497) and those of Bruner (*Ber.*, 1894, **27**, 2106). The method of calculating Σv is that already described.

Eykman (*Zeit. physikal. Chem.*, 1889, **3**, 208, and 1889, **4**, 515) gives the latent heats of fusion of a number of organic compounds, calculated from the molecular depression of their melting points by means of van't Hoff's formula. These, except in cases where the latent heat of fusion has been directly determined, are included in Table V. The values of w, T, and ρ are those given by Eykman, except in the case of acetoxime, where there is an obvious error in the value given for ρ.

TABLE V.

Compound.	w.	T.	ρ.	Σv.	C.
Capric acid	40·6	303	6983	16·27	1·417
Phenylpropionic acid	24·8	322	3720	10·89	1·061
Stearin	47·3	343	42100	83·12	1·477
Ethal	34·3	322	8300	24·81	1·039
Chloral alcoholate	27·0	319	5245	14·88	1·101
Acetoxime	41·4	333	3022	6·79	1·336
Urethylane	48·4	325	3637	5·86	1·909
Diphenylmethane	27·1	300	4553	11·00	1·380
Anethoil	27·9	294	1070	10·93	1·267
Parabromophenol	22·9	337	3961	8·75	1·343
				Mean =	1·333

The 55 organic compounds that have here come under consideration afford generally a confirmation of the principles adopted, and of the relationship which it is sought to establish. Several points, however, in connection with the results obtained deserve special consideration.

Two cases of marked exception occur, the one that of menthol gives a value for $C = 0·584$, which is far too low, and the that of formic acid, the value of C for which, 2·556, is abnormally high. A source of error in the case of menthol arises from the fact that it is impossible at present to correctly estimate the value of Σv for this compound; and this, together with the possibility of error in the latent heat determination, may, perhaps, to some extent, account for the discrepancy observed. At the same time, if menthol may be regarded as a substance of phenolic character, it would probably, like the rest of the phenols, give a low value for C.

In the case of formic acid, the exceptional value for C probably arises almost solely from the method adopted in calculating Σv. The usual formula H·COOH has, of course, been accepted, but several considerations render it probable that to formic acid in the liquid condition some other constitution applies. From the aldehydic character of formic acid alone, it is highly probable that polymerisation might occur at low temperatures, and the work of Ramsay and Shields (Trans., 1893, **63**, 1089) affords evidence that the molecule of liquid formic acid is of a complex nature. Hence to the ordinary molecule either the structure $_{\mathrm{H}}{>}\mathrm{C}{<}^{\mathrm{O-}}_{\mathrm{OH}}$ or even ${>}\mathrm{C}{<}^{\mathrm{OH}}_{\mathrm{OH}}$ may apply. The first of these would give $\Sigma v = 4{\cdot}57$, and the second 4·75, and in either case the value of C would be considerably reduced, although still remaining abnormally high.

The high value which acetic acid gives for C may, perhaps, be explained in similar manner. The results obtained by Ramsay and Shields (*loc. cit.*), the abnormal vapour density, and the formation of the so-called diacetates of the alkali metals, all favour the view that in the liquid state the acetic acid molecule has undergone polymerisation, perhaps to form the grouping $\begin{matrix}\mathrm{CH_3{\cdot}C{\cdot}OH}\\ \mathrm{O}{<}\;{>}\mathrm{O}\\ \mathrm{CH_3{\cdot}C{\cdot}OH}\end{matrix}$ (Meyer and Jacobson, *Lehrbuch der Organischen Chemie*, 1, 321). This would give a value of 5·94 instead of 5·27 to the Σv for acetic acid, and the value for C then becomes 1·616.

The fatty acids generally, with exception of palmitic acid, the latent heat of fusion of which is, perhaps, incorrectly given (compare Bruner, *Ber.*, 1894, **27**, 2105), afford numbers for C which are higher than the mean value. The phenols, on the other hand, yield numbers which are lower than the mean. These facts point to imperfections in the present empirical method of estimating Σv, from which probably arise a large number of the discrepancies observed in the tables. More will be said about this point later on.

Attention should be finally called to the fact that the latent heat of fusion is a quantity the accurate determination of which presents great difficulty, and in the value for which a considerable margin must generally be allowed for experimental error. The direct determinations can fortunately be to a certain extent checked by the cryoscopic method, but in a number of cases the two methods have not given concordant results, thus showing that an error probably exists in either the one result or the other. This is especially marked with palmitic acid, α-naphthylamine and diphenylamine, where the cryoscopic method gives much higher numbers than have been obtained by direct determination. In a still greater number of instances, both methods have not up to the present been applied, the numbers given as the result of direct determination thus lacking this independent confirmation.

Taking these points into account, such variations as appear in the values obtained for C are not surprising, in fact, wider discrepancies might have been expected. Comparing the mean values of C obtained in the different series, we get the following numbers

Metallic elements (10)	$C = 1{\cdot}370$
Non-metallic elements (4)	$C = 1{\cdot}481$
Inorganic compounds (17)	$C = 1{\cdot}340$
Organic compounds. Latent heat obs. (45) ..	$C = 1{\cdot}380$
„ „ „ „ cal. (10) ..	$C = 1{\cdot}333$

Of these, the number obtained in the case of the organic compounds, 1·38, is probably the most accurate, both on account of the large number of compounds taken and the greater ease with which the latent heats could be determined in these cases. Accepting this number, therefore, provisionally as correct, the law which has been enunciated may be expressed as

$$\frac{wA}{Tv} \text{ or } \frac{wM}{T\Sigma v} = 1{\cdot}38,$$

where A is the atomic weight of the element and M the molecular weight of the compound to which the formula is being applied.

By combining this expression with van't Hoff's relationship between the molecular depression of the melting point and the latent heat of fusion, $E = 0{\cdot}02\ T^2/w$, or accurately, $0{\cdot}01976\ T^2/w$, it is possible to calculate the value of E from those of M, T, and Σv, or, in other words, knowing nothing more than the chemical constitution and the melting point of the substance. For E will be found approximately equal to $T \times M/70\ \Sigma v$, or, what is simpler for purposes of calculation, to $0{\cdot}014285 \times T \times M/\Sigma v$.

As might be expected, the differences between the calculated and observed results are found to be large in the case of compounds which give abnormal values for C. Formic and acetic acid give values which are higher, and the phenols give values which are lower than those observed. In this respect, the results are consistent with those previously obtained, and such explanation as has been offered in the former case applies equally in the present instance.

The most important and far-reaching of the applications of the relationship $v\text{M} = \rho = 1{\cdot}38\ \text{T}\Sigma v$ is for the purpose of calculating mutual solubilities, or, what comes to the same thing, of the melting points of mixtures of two compounds which are capable of dissolving the one in the other.

Schroder (*Zeit. physikal. Chem.*, 1893, **11**, 449), and also independently Le Chatelier (*Compt. rend.*, 1894, **118**, 638), have shown that from van't Hoff's theory of osmotic pressure and the nature of solutions there may be deduced the following relationship—

$$\log_e s = \frac{\rho}{2}\,\frac{\text{T} - \text{T}_1}{\text{TT}_1}.$$

Here s is the solubility and represents the number of molecules of the solvent (substance crystallising from the solution) contained in 1 mol. of the solution, T is the melting point of the pure solvent in absolute temperature, T_1 is the melting (or solidifying) point of the solution in absolute temperature, and ρ is the molecular latent heat of fusion of the solvent. (It should be remembered that ρ is a negative quantity.) The expression contains no term relating to the dissolved substance, and a most important point which the study of this relationship has for the first time brought clearly into prominence is that when the solubility is expressed by the number of molecules of the solvent present in 1 mol. of the solution, it is found to be independent of the nature of the dissolved substance, and one and the same solubility curve records the behaviour of a given solvent towards all the compounds which it may be capable of dissolving (see Schroder, *loc. cit.*).

As solvent is here understood the substance which crystallises out first from the liquid mixture on cooling, or the substance the melting point of which may be regarded as undergoing reduction. The definition is the more necessary as this use of the word solvent does not agree fully with the sense in which it is commonly employed. For, in all concentrated solutions of salts and water, or of organic compounds and alcohol from which the salt or the compound crystallises out on cooling, these latter would, according to the definition, be regarded as the solvents, and not the water or the alcohol as is usually taken to be the case.

Applying to Schroder's formula the relationship $\rho = 1{\cdot}38\ \text{T}\Sigma v$, and noting also that the constant 2 in this formula has more accurately the value 1·976, we get (remembering that ρ is negative)

$$\log_e s = -0\ 7\ \Sigma v\,\frac{\text{T} - \text{T}_1}{\text{T}_1},$$

from which also

$$T_1 = \frac{-0{\cdot}7\ \Sigma vT}{\log_e s - 0{\cdot}7\ \Sigma v}.$$

From this it appears, therefore, that knowing nothing more than the chemical constitution and the melting point of a given compound, it should be possible to obtain at once the solubility curve of the compound, and to place on record its general behaviour as a solvent.

An examination of this important relationship is given in the paper which follows this. In conjunction with Miss M. A. Whiteley, I have been recently engaged in determining the melting points of mixtures of organic compounds, and it will be seen that our results afford confirmation of the accuracy of the above formulæ.

Miolati (*Zeit. physikal. Chem.*, 1892, 9, 649) was the first to point out that with the mode of representation here adopted the eutectic point always lies nearest to the melting point of the lower melting constituent of the mixture, or that the eutectic mixture always contains this constituent in the larger proportion. This result may be foreseen from the relationship that has been given. In the case of any two compounds we should have for the one as solvent,

$$T_1 = \frac{-0{\cdot}7\ \Sigma vT}{\log_e s - 0{\cdot}7\ \Sigma v},$$

and for the other as solvent,

$$T_1' = \frac{-0{\cdot}7\ \Sigma v'T'}{\log_e (1 - s) - 0{\cdot}7\ \Sigma v'}.$$

For the eutectic mixture of these two compounds,

$$T_1 = T_1',$$

and therefore the following relationship holds

$$\frac{\Sigma vT}{\Sigma v'T'} = \frac{\log_e s - 0{\cdot}7\ \Sigma v}{\log_e (1 - s) - 0{\cdot}7\ \Sigma v'}.$$

An examination of this formula shows that if $T > T'$ then $s < (1 - s)$, or that in the eutectic mixture the substance of lower melting point is present in the greater proportion. The formula can be made available for calculating eutectic points. An interesting confirmation of its accuracy is afforded by the determination of the eutectic point of mixtures of KNO_3 and $NaNO_3$. Both Schaffgotsch and Carnelley and Thomson state that the eutectic mixture contains about equimolecular proportions of the two salts. Since in this case $\Sigma v = \Sigma v'$ and T differs from T′ by only about 3 per cent. of their actual value, s should be practically equal to $1 - s$, although not absolutely so.*

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* I find by experiment that the eutectic mixture contains 48 mols. KNO_3 to 52 mols. $NaNO_3$, and melts at 220·3°. The calculated values would be 47 mols. KNO_3 to 53 mols. $NaNO_3$, and the melting point 217°.

It is hardly possible to doubt that in the relationship $\rho = 1{\cdot}38\ \Sigma v\mathrm{T}$ we have the expression of some general natural law. The valencies of the elements have been regarded throughout as the determining factors, and it is of course upon these that the calculation of Σv is based. The guiding principle appears to be that equivalent quantities of the elements undergo equal changes of entropy in passing from the solid to the liquid state, this rule being only slightly modified when the elements are contained in their compounds. But the equivalent quantities here spoken of are not what are usually regarded from the chemical point of view as equivalent. They certainly do appear to bear a relationship to the valencies, but this is of a peculiar and merely empirical character, and in some cases, *e.g.*, hydrogen and the halogens, has been virtually abandoned.

Without, however, insisting on the establishment of a general relationship between valency and heat of fusion, the results arrived at in this paper at any rate show that the quantity ρ/T is, in the case of compounds, an additive function, and is made up of certain practically constant values which are peculiar to the atoms of which the molecule is composed. The conclusion to which this result points is a most important and, to some, perhaps, an unexpected one. It is that the change from the solid to the liquid state is one in which the atoms composing the molecule are mainly concerned. Probably, hitherto, the tacit assumption has been that the difference between the liquid and the solid was mainly due to a difference in the size of the molecular aggregates assumed to be present in either case. In other words, that the liquid molecule being M_a and the solid molecule M_b during fusion, the only change was that of $n\mathrm{M}_b$ into $m\mathrm{M}_a$. This view not only receives no confirmation from the results that have been here brought forward, but it is replaced by an entirely different conception, and it is no longer the molecular aggregate, but the simple chemical molecule and its components atoms that are the important factors in the change from the solid to the liquid state.

At the same time, however, the existence of molecular aggregates is not excluded. If the molecular aggregate $n\mathrm{M}$ exists in the solid, the value of ρ for the solid is $n\mathrm{M}w$. But in this case, Σv also becomes $n\Sigma v + a$, where a is the value for the valencies which hold the simple molecules together in the aggregate; in other words, what is usually called the residual valency or affinity. But in most cases a is probably small as compared with $n\Sigma v$, and may be neglected, and therefore $C = n\mathrm{M}w/n\Sigma v\mathrm{T}$, which, since the values of n cancel, is really nothing more than the expression for the simple molecule. It may be, however, that in some cases a is not so entirely negligeable, and some of the discrepancies observed in the values obtained for C may be due to its having been left out of account. That it is necessary in some instances to consider this value has been shown in the cases of formic and acetic acid, and, in fact, if the view here advanced is correct, a method is indicated in the foregoing by means of which the values of *a* could be estimated in certain cases.

The important practical results that follow from the relationship $\rho/\Sigma v\mathrm{T} = C$ are those which have been indicated, namely, the possibility of calculating the molecular depression of the melting point and the solubility of any given compound in any given solvent as soon as the chemical constitution and the melting point are known.

Note.—Since the above was written, it has been shown by Traube that a relationship in all probability exists between the valency and the atomic volume of an element (*Ber.*, 1894, **27**, 2178). It can be shown thermodynamically that the latent heat of fusion is a function of the molecular volume of a compound, hence of the sum of the atomic volumes, and from this it may be argued that the latent heat of fusion must also be a function of the sum of the valencies of the atoms in the molecule (compare *Ber.*, 1895, **28**, 148). The establishment of such relationships as these promises to throw considerable light in the future on the obscure question of the nature of valency.

XXXIX.—*The Melting Points of Mixtures.*

By HOLLAND CROMPTON and Miss M. A. WHITELEY.

CASES in which the melting points of mixtures of two mutually soluble substances in all proportions have been investigated are not at present very numerous. The discovery by Raoult of the connection between the depression of the melting point of the solvent and the molecular weight of the dissolved substance, and the generalisation of van't Hoff with respect to dilute solutions, led to a large number of observations being made on the melting points of solutions, but these were almost invariably confined to small dilutions. Étard (*Compt. rend.*, 1892, **115**, 950) has pointed out that the curve for the mutual solubility of two substances, one in the other at different temperatures, is the locus of the melting points of mixtures of the two substances; it is, however, only in very few instances that a complete solubility curve has been obtained, the actual observations being in most cases confined to a small portion of the (theoretically) possible curve, and dilute solutions being here also usually dealt with. From this point of view, therefore, the mode of investigation has been one-sided, and if not leading directly to erroneous views, is not calculated to elucidate the more general problem of solution. For it need hardly be pointed out that it is only by studying the whole range of solubility, dealing with concentrated as well as dilute solutions, that it is possible to hope to arrive at any satisfactory conclusions with reference to these phenomena.

We have for some time past been engaged in determining the melting points of mixtures of two substances in various proportions. The work (which we are still continuing) has unfortunately been much interrupted, and we wish the present results to be regarded as preliminary only, but as they lend support to certain important general conclusions, we have thought it would be of interest to bring them forward at this stage.

Le Chatelier, who has of late been investigating the fusing points of saline mixtures, shows that in mixtures three general cases may be distinguished (*Compt. rend.*, 1894, **118**, 709).

1. The substances solidify to form isomorphous mixtures of variable composition.

2. Each substance solidifies separately from the mixture.

3. The two substances combine and solidify as a compound of definite composition.

With one exception, most probably belonging to the class of isomorphous mixtures, we have had up to the present only mixtures of the second kind to deal with.

To such mixtures the following general relationship applies (see preceding paper),

$$\log_e s = \frac{\rho}{1{\cdot}98}\,\frac{T - T_1}{TT_1},$$

a relationship that has already been obtained independently by both Schröder (*Zeit. physikal. Chem.*, 1893, **11**, 449) and Le Chatelier (*Compt. rend.*, 1894, **118**, 638). Since this equation contains no term relating to the dissolved substance, the values of T_1 will always be the same for the same values of s in the case of any one particular solvent, or, in other words, if the melting points, T_1, of any solutions containing this solvent are plotted against the values of s, one and the same curve should (theoretically) always be obtained. Further, if the latent heat of fusion is known, the values of T_1 can be calculated from the known values of s and T, and thus the melting-point curve for any solvent can be obtained. By solvent is to be understood that constituent of a mixture which first crystallises out on cooling.

Now it has been shown by one of us (preceding paper) that the molecular latent heat of fusion $\rho = 1{\cdot}38\,\Sigma v T$, where Σv is a number bearing a simple relationship to the valencies of the atoms present in the molecule, and easily calculated when the constitution of the substance under examination is known. The introduction of this value for ρ into the formula previously deduced, leads to

$$\log_e s = -0{\cdot}7\,\Sigma v\,\frac{T - T_1}{T_1}$$

or

$$T_1 = \frac{-0{\cdot}7\,\Sigma v T}{-0{\cdot}7\,\Sigma v + \log_e s}.$$

The values of T_1 can, therefore, be at once calculated for any solvent when the melting point and the chemical constitution of the substance are known.

Our results enable us to put this generalisation to the test of experiment, and to ascertain in how far it may be regarded as applicable under ordinary conditions. A close agreement between the calculated and observed results is, of course, hardly to be looked for, as the above relationship between ρ and Σv is not an absolutely exact one, and holds only approximately. We have for this reason, and also because the quantities of material at our command were limited, adopted the ordinary capillary-tube method for determining the melting points of the mixtures. This method, as is well known, gives results which are less accurate than those obtained by direct immersion of the thermometer in the mixture, but that they are of sufficient exactness for the purpose in view will be seen later on.

The mixtures were made by weighing out the requisite quantities on a watch-glass, fusing them together, and then grinding the fused mass in a mortar. Such a mixture does not melt sharply, but usually the melting takes place within a limit of about 3°. The upper limit, or the point at which the whole of the mixture becomes liquid, has in each case been taken as the melting point. The thermometers used were graduated in $\frac{1}{10}$°, five or six different observations were made with each mixture and the mean of these taken.

The results are contained in the following tables. The first two columns of these tables give the composition of the mixtures in what may be termed molecular percentages, or the number of molecules of each constituent present in 100 molecules of the mixtures. In the case of the solvent this number is 100*s*. In the third column are placed the observed melting points, *t*, and in the fourth the values of $T_1 - 273$; T_1 being calculated from those of *s*, T, and Σv in the manner described. The fifth column contains the differences between the numbers in the third and those in the fourth column, or the differences between the observed and calculated melting points. The explanation of the numbers in the sixth and seventh columns is given later on. The dotted line drawn across each table indicates the position of the eutectic point and consequent change of solvent.

I. *Metanitraniline and Metadinitrobenzene.*

Metanitraniline, m. p. = 114°. Metadinitrobenzene, m. p. = 90·2°.
" Σv = 7·52. " Σv = 8·12.

Molecular percentage.		M. p. obs. *t*.	T_1-273.	Diff.	M. p. cal. *t'*.	$\Delta t-t'$ obs.—cal.
Nitraniline.	Dinitrobenzene.					
	(solvent)					
10	90	82·7	83·6	0·1	—	—
20	80	76·1	76·5	−0·4	—	—
30	70	68·0	68·4	−0·4	—	—
35	65	63·3	64·6	−1·3	—	—
(solvent)						
40	60	62·4	56·6	5·8	62·7	−0·3
41	59	64·1	57·9	6·2	63·9	0·2
45	55	69·6	63·0	6·6	68·4	1·2
50	50	73·5	69·0	4·5	73·8	−0·3
55	45	78·0	74·5	3·5	78·7	−0·7
60	40	83·6	79·8	3·8	83·4	0·2
70	30	93·5	89·4	4·1	92·0	1·5
80	20	100·5	98·3	2·2	100·0	0·5
90	10	107·5	106·4	1·1	107·2	0·3

II. *Metanitraniline and Acetanilide.*

Metanitraniline, m. p. = 114°. Acetanilide, m. p. = 113·5°.
" Σv = 7·52. " Σv = 8·66.

Molecular percentage.		M. p. obs. *t*.	T_1-273.	Diff.	M. p. cal. *t'*.	Δ_t-t' obs.—cal.
Nitraniline.	Acetanilide.					
	(solvent)					
20	80	99·3	99·8	−0·5	101·0	−1·7
30	70	93·2	92·0	1·2	93·9	−0·7
40	60	85·5	83·5	2·0	86·2	−0·7
45	55	83·3	78·8	4·5	82·0	1·3
(solvent)						
50	50	82·7	69·0	13·7	83·5	−0·8
55	45	88·0	74·5	13·5	87·1	0·9
60	40	91·2	79·8	11·4	90·8	0·4
70	30	97·3	89·4	7·9	97·3	0·0
80	20	103·0	98·3	4·7	103·3	−0·3

III. *Acetanilide and Metadinitrobenzene.*

Acetanilide, m. p. = 113·5°. Metadinitrobenzene, m. p. = 90·2°.
" Σv = 8·66. " Σv = 8·12.

Molecular percentage.		(M. p.) T obs. t.	T_1-273.	Diff.	(M. p.) T cal. t'.	$\Delta_{t-t'}$ obs.—cal.
Acetanilide.	Dinitrobenzene.					
	(solvent)					
10	90	85·6	83·6	2·0	86·0	−0·4
20	80	80·2	76·5	3·7	80·5	−0·3
30	70	75·5	68·4	7·1	74·7	0·8
35	65	71·5	64·6	6·9	72·1	−0·6
(solvent)						
40	60	70·0	62·7	7·3	69·3	0·7
50	50	79·5	73·9	5·6	79·1	0·4
60	40	86·8	83·5	3·3	87·4	−0·6
80	20	101·1	99·8	1·3	101·6	−0·5

IV. *Acetanilide and α-Dinitrophenol.*

Acetanilide, m. p. = 113·5°. α-Dinitrophenol, m. p. = 112·5°.
" Σv = 8·66. " Σv = 9·81.

Molecular percentage.		M. p. obs. t.	T_1-273.	Diff.	M. p. cal. t'.	$\Delta_{t-t'}$ obs.—cal.
Acetanilide.	Dinitrophenol.					
	(solvent)					
17·68	82·32	104·3	101·9	2·4	103·9	0·4
26·92	73·08	99·5	95·7	3·8	98·9	0·6
36·44	63·56	94·4	88·6	5·8	93·2	1·2
41·29	58·71	89·1	84·7	4·4	90·0	−0·9
46·23	53·77	86·0	80·6	5·4	86·7	−0·7
50·00	50·00	83·3	77·2	6·1	84·0	−0·7
(solvent)						
56·33	43·67	79·5	80·1	−0·6	—	—
65·00	35·00	88·3	87·8	0·5	—	—
77·49	22·51	97·0	97·9	−0·9	—	—
85·00	15·00	103·4	103·5	−0·1	—	—

V. α-Dinitrophenol and Orthonitrophenol.

α-Dinitrophenol, m. p. = 112·5°. Orthonitrophenol, m. p. = 46·2°.
„ Σv = 9·81. „ Σv = 8·43.

Molecular percentage.		M. p. obs. t.	$T_1 - 273$.	Diff.	M. p. cal. t'.	$\Delta_t - t'$ obs. − cal.
Dinitrophenol.	o-Nitrophenol.					
	(solvent)					
10	90	41·0	40·6	0·4	41·1	−0·1
15	85	38·6	37·6	1·0	38·4	0·2
(solvent)						
20	80	40·0	39·3	0·7	—	—
25	75	51·6	47·8	3·8	—	—
30	70	55·8	55·2	0·6	—	—
38·64	61·36	64·8	65·6	−0·8	—	—
50	50	82·3	77·2	5·1	—	—
60	40	89·7	85·8	3·9	—	—
65	35	90·9	89·7	1·2	—	—
70	30	96·4	93·4	3·0	—	—
75	25	100·9	97·0	3·9	—	—
80	20	105·2	100·4	4·8	—	—
90	10	108·8	106·7	2·1	—	—

VI. α-Naphtol and β-Naphtol.

α-Naphtol, m. p. = 95·5°. β-Naphtol, m. p. = 122·2°.
„ Σv = 9·86. „ Σv = 9·86.

Molecular percentage.		M. p. obs. t.	$T_1 - 273$.	Diff.	M. p. cal. t'.	$\Delta_t - t'$ obs. − cal.
α-Naphtol.	β-Naphtol.					
	(solvent)					
10	90	116·5	116·3	0·2	—	—
20	80	109·5	109·8	−0·3	—	-
30	70	102·7	102·8	−0·1	—	—
40	60	93·9	95·0	−1·1	—	—
50	50	85·1	86·1	−1·0	—	—
60	40	75·8	75·9	−0·1	—	—
(solvent)						
70	30	79·1	77·4	1·7	79·6	−0·5
80	20	85·1	84·0	1·1	85·4	−0·3
84·9	15·1	89·1	87·0	2·1	88·1	1·0

VII. *α-Naphtol and Naphthalene.*

α-Naphtol, m. p. = 95·5°. Naphthalene, m. p. = 79·8°.
" Σv = 9·86. " Σv = 8·17.

Molecular percentage.		M. p. obs. *t*.	$T_1 - 273$.	Diff.	M. p. cal. *t′*.	$\Delta_t - t'$ obs. − cal.
α-Naphtol.	Naphthalene.					
	(solvent)					
10	90	74·8	73·4	1·4	75·6	−0·8
20	80	71·2	66·5	4·7	71·0	0·2
30	70	65·7	59·1	6·6	66·2	−0·5
35	65	64·4	55·1	9·3	63·6	0·8
38·9	61·1	61·7	52·3	9·4	61·7	0·0
……	……	……	……	……	……	……
(solvent)						
40	60	62·2	52·4	9·8	61·9	0·3
50	50	69·6	61·9	7·7	69·3	0·3
60	40	74·5	70·1	4·4	75·7	−1·2
70	30	80·8	77·4	3·4	81·4	−0·6
81·8	18·2	87·5	85·0	2·5	87·3	0·2
90	10	92·5	90·0	2·5	91·2	1·3

In Table VIII are given the melting points of mixtures of β-naphtol and naphthalene. These mixtures differ from the above, as the addition of β-naphtol to naphthalene does not lower, but raises the melting point of the latter. The melting points of the mixtures lie upon a continuous curve joining the melting points of the constituents (van Bijlert, *Zeit. physikal. Chem.*, 1891, 8, 343). We have

VIII. *β-Naphtol and Naphthalene.*

β-Naphtol, m. p. 122·2°. Naphthalene, m. p. 79·8°.

Molecular percentage.		M. p. obs. *t*.	Mean m. p.	Diff.	M. p. cal. *t′*.	$\Delta_t - t'$ obs. − cal.
β-Naphtol.	Naphthalene.					
	(solvent)					
10	90	84·6	84·0	0·6	84·2	0·4
20	80	88·6	88·3	0·3	88·8	−0·2
30	70	94·0	92·5	1·5	94·1	−0·1
……	……	……	……	……	……	……
(solvent)						
40	60	98·9	96·8	2·1	98·3	0·6
50	50	103·9	101·0	2·9	103·5	0·4
60	40	107·2	105·2	2·0	108·2	−1·0
70	30	111·1	109·5	1·6	112·2	−1·1
80·25	19·75	114·1	113·8	0·3	115·7	−1·6
90	10	119·5	118·0	1·5	119·2	0·3

here probably a case of an isomorphous mixture, similar to those investigated by Küster (*Zeit. physikal. Chem.*, 1890, **5**, 601, and 1891, **8**, 577). If the melting points are plotted against the molecular percentages, a straight line curve should therefore be obtained. In the table (VIII), the fourth column contains numbers calculated on this assumption in place of values of $T_1 - 273$.

A comparison of the values of $T_1 - 273$ with the observed melting points shows that in certain cases there is coincidence within the possible error of experiment. This holds for the following pairs of substances.

Solvent:	Metadinitrobenzene.	Dissolved substance:	Metanitraniline.
,,	Acetanilide.	,, ,,	Dinitrophenol.
,,	Orthonitrophenol	,, ,,	,,
,,	α-Naphtol	,, ,,	β-Naphtol.
and partially			
Solvent:	Dinitrophenol	,, ,,	Orthonitrophenol.

The results in this last instance are very irregular from some cause which we are at present quite unable to explain.

In the majority of cases, however, the observed melting points differ considerably from the values calculated for $T_1 - 273$, the differences lying altogether outside the limits allowable for error of experiment. It will be noticed also that the observed values are invariably higher than the calculated, and that the differences as a rule increase with the concentration of the solutions. These discrepancies might be due either to some incorrect value being assigned to Σr, and consequently to ρ, in the cases in question, or to some disturbing influence affecting the application of the general relationship.

But that they cannot be referred to such errors either in the Σr, or in ρ, is shown on comparing the numbers obtained with one and the same solvent when the dissolved substance is varied. Such a variation should, according to theory, have no effect on the observed melting points for mixtures of the same molecular percentage composition. In the following tables the melting points of mixtures of this kind are compared, and that there is a marked influence due to variation of the dissolved substance is at once apparent.

Solvent: Metanitraniline.

Mol. percentage.	Metadinitrobenzene.	Acetanilide.
80	M. p. = 100·5°	M. p. = 103·0°
70	93·5	97·3
60	83·6	91·2
55	78·0	88·0
50	73·5	82·7

Solvent: Acetanilide.

Mol. percentage.	Metanitraniline.	Metadinitrobenzene.
80	M. p. = 99·3°	M. p. = 101·1°
60	85·5	86·8

Solvent: α-Naphtol.

Mol. percentage.	Naphthalene.	β-Naphtol.
80	M. p. = 87·0°	M. p. = 85·1°
70	80·8	79·1

The want of agreement between the values of $T_1 - 273$ and the observed melting points is not one, then, which can be explained by assuming the error to lie in the number deduced for Σv, or for ρ, but must be due to a disturbing influence affecting the application of the general relationship. The nature of this disturbing influence is sufficiently indicated by the character of the differences between the observed and calculated values. For it has been pointed out that the observed are always higher than the calculated values, where any appreciable difference is noticed, and further that the differences increase with the increase in the relative quantity of the dissolved substance present. Cases of this kind have already been frequently noticed in cryoscopic determinations, in fact, strictly speaking, they are probably the rule rather than the exception. The explanation has been given by van't Hoff (*Zeit. physikal. Chem.*, 1890, **5**, 322), and is found in the fact that whereas theoretically the pure solvent is supposed to crystallise out from a solution when the solidifying (or melting) point is reached, practically a certain quantity of the dissolved substance usually crystallises out along with the solvent, forming with the latter a solid solution. The effect of this is to reduce the osmotic pressure of the solution, and, therefore, to raise the melting point. The true melting point therefore becomes $T_1 + \tau$, where τ represents the rise due to the influence in question, or in fact $\tau = t - (T_1 - 273)$.

Van't Hoff further shows that, at any rate in dilute solution, the raising of the theoretical melting point, or the quantity τ, is proportional to the theoretical depression of the melting point $T - T_1$. If we assume as a first approximation, what is probably not far from the truth, that this relationship also holds for concentrated solutions, since

$$T - T_1 = \frac{1{\cdot}98T}{\rho} T_1 \log_e s = \text{const. } T_1 \log_e s$$

for any particular solvent,

$$\tau = c\, T_1 \log_e s,$$

where c is a constant. The true melting point of the solution is therefore given by the expression

$$t' = \text{m. p. cal.} = T_1 + c\,T_1 \log_e s - 273.$$

It is in this way that the numbers contained in the sixth column of the tables already given have been calculated. The values for c in each case have been calculated empirically from those of τ, and are as follows (the numbers are, of course, negative)—

Solvent.	Dissolved substance.	c.
Metanitraniline	Metadinitrobenzene	0·0203
„	Acetanilide	0·0610
Metadinitrobenzene	„	0·0516
Acetanilide	Metanitraniline	0·0151
„	Metadinitrobenzene	0·0215
α-Dinitrophenol	Acetanilide	0·0280
Orthonitrophenol	α-Dinitrophenol	0·0160
α-Naphtol	Naphthalene	0·0320
„	β-Naphtol	0·0180
Naphthalene	α-Naphtol	0·0600
„	β-Naphtol	0·2950
β-Naphtol	Naphthalene	0·0700

In the seventh column of the tables are placed the differences, Δ obs.—cal., between the observed melting points and those calculated in the above manner. These differences do not in all probability exceed the limit which must be admitted for possible error in the determinations by the method adopted, and, as would be expected in such a case, they are sometimes positive and sometimes negative. The calculated values therefore agree with those observed for the melting points within the limits allowable for experimental error, and this holds even in the case of mixtures of β-naphtol and naphthalene, where probably the substances dealt with form an isomorphous mixture. Indeed, in this case, the melting points calculated by the method indicated agree far more closely with the observed than those calculated on the assumption that the melting point curve is a continuous straight line.

From the behaviour, then, of the eight different substances which we have had under examination, and the 16 different solutions formed from them, we come to the following conclusions—

1. For normal solutions, in which on cooling the solvent alone first crystallises out, the relationship $\log_e s = \frac{\rho}{1{\cdot}98}\,\frac{T - T_1}{TT_1}$ holds for all concentrations.

2. For ρ, the value 1·38 ΣvT can be substituted, and the relationship which one of us has sought to establish between the latent heat of

fusion of a molecule and the valencies of the component atoms is confirmed by the result of these experiments.

3. The abnormal behaviour of certain solutions may be explained by supposing, that from such solutions the solvent does not crystallise out alone, but forms with the dissolved substance a solid solution, the observed melting points being in these cases invariably higher than the calculated.

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XL.—*Electrolysis of Potassium Allo-ethylic Camphorate.*

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It has been shown by one of us (Walker, Trans., 1893, **63**, 495) that when the sodium ortho-ethylic salt of camphoric acid is subjected to electrolysis in strong aqueous solution, the chief product is the ethylic salt of an unsaturated monobasic acid $C_9H_{14}O_2$. From the behaviour of its dibromide, this campholytic acid would appear to be an $\alpha\beta$-unsaturated acid, a fact which has a direct bearing on the position of the carboxyl groups in the camphoric acid molecule.

It appeared to us of interest to perform the electrolysis of the isomeric sodium allo-ethylic camphorate, in which the sodium atom and the ethyl group have exchanged places, in order to obtain if possible an isomeride of campholytic acid, and to investigate the properties of its dibromide. We have in reality obtained from the corresponding potassium salt more than one isomeride, and the results of the research, so far as it is completed, are given below.

The potassium allo-ethylic camphorate used in the electrolysis was prepared as follows. Twenty-three grams of sodium were dissolved in 350 c.c. of absolute alcohol, and to this solution of sodium ethoxide there were gradually added 182 grams of powdered camphoric anhydride, which dissolved with evolution of heat. The alcoholic solution of sodium ortho-ethylic camphorate obtained in this way was heated with ethylic bromide in order that diethylic camphorate might be produced. Bruhl (*Ber.*, 1891, **24**, 3408) recommends heating the reacting substances for 10 hours at 130° in a sealed tube. This is a somewhat troublesome operation when large quantities of solution have to be dealt with, but as we have found that the action proceeds equally well at 100°, the following process may be adopted. 100 c.c. of the alcoholic solution are introduced into a soda-water bottle with a quantity of ethylic bromide 10 per cent. in excess of the theoretical amount (1 mol. to 1 atom sodium). The bottle is well corked and heated in a water bath for 6 hours, the action being then practically at an end, as we found by weighing the sodium bromide which had separated from the alcoholic solution on cooling. In one case, for example, after six hours' heating, the amount of sodium bromide collected was 17 grams, the theoretical amount being 17 7 grams. After the action is complete, the bulk of the alcohol is distilled off on the water bath and water added. The aqueous solution gives a neutral reaction with litmus. The diethylic salt is separated by means of ether, which is washed first with water containing a little caustic soda, and lastly with pure water; after drying with calcium chloride and distilling off the ether, the residue is distilled under diminished pressure. The yield of diethylic camphorate of constant boiling point is rather more than equal to the amount of camphoric anhydride taken, or 73 per cent. of the theoretical.

The diethylic salt (1 mol.) is mixed with potassium hydroxide (1 mol.) dissolved in eight times its weight of absolute alcohol, and the mixture allowed to remain overnight. It is then heated for half an hour on the water bath to complete the half-saponification; the alcohol is distilled off, and the residue dissolved in two-thirds of its own weight of water, and the aqueous solution is shaken up with ether in order to remove a small quantity of unaltered diethylic camphorate. After the ethereal layer has been separated, and the aqueous layer heated to remove the ether dissolved in it, the solution of potassium allo-ethylic camphorate is ready for electrolysis.

The manner of conducting the electrolysis diverged somewhat from that previously practised. Two nickel crucibles, each of 75 c.c. capacity, were employed as cathodes, and in them the solution to be electrolysed was placed. By means of triangles made of stout insulated copper wire, wrapped round with cord, these crucibles were held in position in a shallow cylindrical metal dish, through which a stream of cold water was kept constantly flowing, the level of the outflow being only slightly beneath that of the mouths of the crucibles. Care must be taken that the crucibles are thoroughly insulated and at no part touch the metal dish. The anodes, as before, were constructed of stout platinum wire in the form of a spiral with a diameter about 1 cm. less than the diameter of the crucible. The crucibles were connected up in series with each other, and with an electrolytic resistance. The current we employed was much greater than that used by Crum Brown and Walker (*Annalen*, 1890, 261, 112), being derived directly from a dynamo with a voltage of about 100. The electrolytic resistance consisted of a dilute solution of sodium sulphate contained in a large beaker with electrodes of platinum foil. This solution was allowed to boil when the current passed, and the resistance could be easily regulated by varying the depth of immersion of the electrodes, the distance between them, or the concentration of the solution. As great a current was allowed to pass as was consistent with the contents of the crucibles being kept below 40° by means of the cooling apparatus. Each charge was electrolysed for 45 minutes, after which the contents of the crucibles were removed and allowed to settle in a tall separating cylinder, a fresh charge being then introduced. When all the original solution of the potassium ethylic salt had been treated in this way, the layer of ethereal liquid, which had floated to the surface, was drawn off and the solution again submitted to electrolysis for 30 minutes. A considerable additional quantity of ethereal product was thus obtained, but practically no result was obtained on a third electrolysis. The spent solution was finally extracted with ether, the whole of the ethereal portions united, dried with calcium chloride, and freed from ethylic ether on the water bath. By working with a powerful current in the above manner, the rate of the electrolysis is greatly increased, so that several hundred grams of the ethereal product can be obtained in the course of two or three days. As in the case of the sodium ortho-ethylic salt, a certain irregularity of the yield under precisely similar conditions was experienced, but slight alterations of concentration, &c., were again sufficient to secure the desired result. The vapours evolved on electrolysis have a powerful and persistent odour, but are by no means so unpleasant as those formed with the ortho-ethylic salt.

From the spent aqueous solution, a large quantity of hydrogen allo-ethylic camphorate may be recovered by acidification and extraction with ether, and this may be converted into a pure solution of potassium ethylic salt of the proper concentration, and again electrolysed. Taking this recovered portion into consideration, the actual yield on electrolysis is very satisfactory, amounting almost to 80 per cent. of that theoretically possible. Thus 600 grams of camphoric acid yielded 522 grams of camphoric anhydride, which afforded 547 grams of diethylic camphorate. After half-saponification, 30 grams of this ethereal salt were recovered unchanged, so that the aqueous solution contained 530 grams of potassium ethylic salt. On completion of the electrolysis, 128 grams of hydrogen ethylic camphorate were recovered, corresponding to 145 grams of potassium ethylic salt, so that 385 grams had been electrolytically decomposed. This quantity would yield 265 grams of ethereal product of the ordinary type, and 210 grams were actually obtained. The amount of decomposition by oxidation is thus very small.

The course of the electrolysis was normal, the chief ethereal products, on investigation, proving to be isomeric unsaturated ethylic salts of the formula $C_{11}H_{18}O_2$, and a saturated diethylic salt of the formula $C_{22}H_{38}O_4$, formed according to the equations

$$\text{I. } 2C_8H_{14}\Big<\begin{matrix}COOEt\\COO\end{matrix} = C_8H_{14}\Big<\begin{matrix}COOEt\\COOH\end{matrix} + C_8H_{13}\cdot COOEt + CO_2$$

and

$$\text{II. } 2C_8H_{14}\Big<\begin{matrix}COOEt\\COO\end{matrix} = EtOOC\cdot C_8H_{14}\cdot C_8H_{14}\cdot COOEt + 2CO_2.$$

In accordance with the nomenclature suggested for the ortho-compounds, these substances may be termed ethereal salts of allo-campholytic acids and of allo-camphothetic acid respectively.

In order to isolate the ethereal salts, the whole product of electrolysis was distilled under a pressure of 15 mm., and the portion boiling below 140° was then refractionated at the ordinary atmospheric pressure.

Allo-ethylic Campholytate.

By far the greater portion (67 grams) of the liquid of lower boiling point passed over between 195° and 210°, and on repeated refractionation 45 grams of a colourless oil was obtained boiling constantly at 204°. This oil, on analysis, proved to have the composition $C_{11}H_{18}O_2$.

0·1565 gave 0·4153 CO_2 and 0·1410 H_2O. C = 72·36; H = 10·01.

$C_{11}H_{18}O_2$ requires C = 72·52; H = 9·89 per cent.

The sp. gr. of this ethereal salt is 0·951 at 16°/4°. It is optically active, and at 19° has the specific rotation $[\alpha]_D = +39\cdot1$, the corresponding value for the isomeric ethylic campholytate being $[\alpha]_D = +5\cdot04$.

It readily decolorises a solution of bromine in carbon bisulphide in the cold, and when brominated in the dark under the conditions recommended by Wislicenus (*Annalen*, 1892, **272**, 13) yields a dibromide.

Dibromide of Diethylic Allo-campholytate, $C_{11}H_{18}O_2Br_2$.

This is a pale yellow liquid which gives off hydrogen bromide at the ordinary temperature and cannot be distilled, either by itself or with steam, without undergoing decomposition. For this reason, the quantity of bromine found on analysis is always less than that required by theory.

0·296 gave 0·312 gram AgBr. Br = 44·6.

$C_{11}H_{18}O_2Br_2$ requires Br = 46·8 per cent.

The oil has the density 1·496 at 20°/4°, and is miscible with the ordinary organic solvents.

Allo-campholytic acid.

Twenty-two grams of the ethylic salt were boiled for three hours with 12 grams of potassium hydroxide in alcoholic solution. The alcohol and unaltered ethylic salt were distilled off with steam, and the residual aqueous solution acidified with hydrochloric acid. An oily acid separated, which was extracted with ether; the ethereal solution was then washed with water in order to remove hydrochloric acid, the ether evaporated, and the residue distilled with steam. Oily drops came over slowly, and a small quantity of tarry matter remained in the distilling flask. The aqueous distillate was neutralised with sodium carbonate, evaporated to a small bulk, acidified, and extracted with ether. On drying the ethereal solution with calcium chloride and distilling off the ether, 7 grams of an almost colourless oil were obtained, which was then fractionated under the ordinary pressure. It began to boil at 210°, but most of it came over at 233—235°. This is the boiling point of Fittig and Woringer's campholactone (*Annalen*, 1885, **227**, 10), which is isomeric with campholytic acid, but as the oil we obtained was readily soluble in sodium carbonate solution, very sparingly soluble in water, and did not crystallise after long exposure to the temperature of a good freezing mixture, it was evident that we were here dealing with a different substance.

Analysis of the oil yielded the following results.

0·2010 gave 0·5160 CO_2 and 0·1650 H_2O. C = 70·01; H = 9·11.
$C_9H_{14}O_2$ requires C = 70·13; H = 9·09 per cent.

The substance is, therefore, an isomeride of campholytic acid.

It is miscible with the ordinary organic solvents, and has the density 0·993 at 18°/4°. It is optically active, the specific rotation being $[\alpha]_D = +57·4$ at 12°, whilst the value for the isomeric campholytic acid is $[\alpha]_D = -5·0$.

The calcium salt was prepared by neutralising the acid by calcium carbonate; it is moderately soluble in water, the cold concentrated solution becoming turbid on warming. On evaporating a dilute solution on the water bath, a crystalline scum is formed; these crystals were collected, and the water in them determined. The remaining solution was then evaporated to dryness at the ordinary temperature in an exhausted desiccator, and the amount of water determined in the crystalline residue.

I. 0·2412 lost 0·0232 at 120° and gave 0·0876 $CaSO_4$.
II. 0·0976 „ 0·0089 „ „ 0·0340 „

	Calculated for $Ca(C_9H_{13}O_2)_2,2H_2O$.	Found. I.	Found. II.
Ca	10·47	10·65	10·3
H_2O	9·42	9·61	9·1

The calcium salt thus contains 2 mols. of water, whether crystallised at 100° or at the ordinary temperature.

A strong solution of the sodium salt gives precipitates with silver nitrate, lead nitrate, copper sulphate, and zinc nitrate. The silver salt does not blacken readily on boiling, but does so rapidly on exposure to sunlight. The zinc salt is moderately soluble in cold water, the saturated solution becoming turbid on heating. It is very soluble in ether.

When allo-campholytic acid is treated with sulphuric acid (1 vol. H_2SO_4 sp. gr. 1·84 : 1 vol. H_2O), as described by Fittig (*Annalen*, 1894, **283**, 51), it is to a great extent carbonised, and little can be extracted from the product of the action. If, however, the mixture, instead of being boiled, was heated on the water bath for ten minutes, it became merely red; after cooling and dilution it was extracted with ether, and the ethereal layer shaken up several times with a dilute solution of sodium carbonate. After drying with calcium chloride, the ether was evaporated and an oily residue obtained, which, on standing, deposited well-formed crystals; these crystals possessed a strong odour of camphor, and melted at 50°. The substance was moderately soluble in cold water, the solution becoming turbid on gently warming, and again clear as the boiling point was approached: the phenomena were reversed on cooling. This behaviour left no doubt that the substance was the campholactone described by Fittig and Woringer (*Annalen*, 1885, **227**, 10). The lactone which they obtained can be prepared from the isomeric lauronolic acid $C_9H_{14}O_2$ by treatment with sulphuric acid, so it was of importance to determine if allo-campholytic acid was identical with lauronolic acid. The description they give was found scarcely sufficient for purposes of identification, so a quantity of lauronolic acid was prepared in the manner described by Aschan (*Ber.*, 1894, **27**, 3504), in order that a direct comparison might be made. This comparison sufficed to establish the non-identity of the two substances. In the first place, the specific rotation of lauronolic acid is $[\alpha]_D = +17$, that of allo-campholytic acid being $+57$. The calcium salt of lauronolic acid crystallises, according to Fittig and Woringer, and also according to Aschan, with $3H_2O$, whilst the salt of our acid crystallises with $2H_2O$. Lauronolic acid on treatment with bromine is converted into a bromolactone, $C_9H_{13}BrO_2$, m. p. 187°, whilst allo-campholytic acid under the same conditions gives, for the most part, a liquid dibromide.

Aschan obtained from lauronolic acid a solid amide, melting at 72°: allo-campholytic acid, on treatment with phosphorus pentachloride and ammonia, yields a liquid amide.

Allo-campholytic acid is thus distinct from lauronolic acid, but would seem to be identical with the acid obtained by Noyes from the chloride of amino-lauronolic acid by the action of sodium nitrite. The calcium salt of this acid (*Amer. Chem. J.*, 1894, **16**, 508) crystallises with $2H_2O$, and the zinc salt is soluble in ether. In a private communication, Prof. Noyes also states that his acid yields campholactone on treatment with dilute sulphuric acid (1 : 1), and that its amide is liquid so far as he has observed. In these points it therefore shows a strong resemblance to allo-campholytic acid.

Dibromide of Allo-campholytic acid.—Five grams of allo-campholytic acid in 20 c.c. of carbon bisulphide were gradually added to 7 grams of dry bromine dissolved in 20 c.c. of carbon bisulphide. The mixture was allowed to remain over-night, and the carbon bisulphide removed on the following morning by a stream of dry air. The residue was mostly liquid, but contained a small quantity of a crystalline substance. The liquid was washed away from the crystals by a little light petroleum, and the residual solid recrystallised from warm benzene. The crystalline substance then melted at 184°, blackening at the same time, and was probably the bromolactone described by Aschan (*loc. cit.*), which melts at 187°. The small quantity, however, precluded an accurate analysis.

The liquid obtained after evaporation of the light petroleum gave the following numbers by the Carius method.

0·4399 gave 0·5284 AgBr. Br = 51·1.
0·4134 „ 0·4912 AgBr. Br = 50·8.
$C_9H_{14}Br_2O_2$ requires Br = 50·9 per cent.

The liquid was thus a dibromide formed by the direct addition of bromine to the unsaturated acid. The action of alkalis on this dibromide will be described in a subsequent paper.

Solid Acids.—From the ethylic salt which was recovered on saponification of the ethereal product boiling at 204°, a new acid was obtained on prolonged treatment with very concentrated alcoholic potash. The potassium salt separated from the alcoholic solution, and, on acidification with hydrochloric acid, yielded a solid acid, which was volatile with steam; on recrystallisation from benzene and light petroleum, it melted at 158°. It is an unsaturated acid isomeric with allo-campholytic acid.

Another acid, melting at 146°, was obtained along with a liquid acid from the ethereal product boiling at 220—230°. These substances, together with the fractions boiling between 110° and 240°, under 15 mm. pressure, are being investigated, and will form the subject of a future communication.

Diethylic Allo-camphothetate.

The tarry residue left on distilling the ethereal product of electrolysis up to 240°, under 15 mm. pressure, became partially solid on long standing. It was spread in a thin layer on porous plates which, after several weeks, absorbed the bulk of the tar, a crystalline substance being left. This was scraped off and spread on a fresh porous surface; it soon became pale brown, and was then recrystallised repeatedly from light petroleum. When the solvent was allowed to evaporate very slowly, the substance separated in the form of large rhombic tables; it melts at 67—68°, and is insoluble in water, but soluble in all ordinary organic solvents. The following results were obtained on analysis.

I. 0·0851 gave 0·2260 CO_2 and 0·0813 H_2O. C = 72·42; H = 10·61.
II. 0·1026 „ 0·2712 „ „ 0·0987 H_2O. C = 72·09; H = 10·67.
$C_{22}H_{38}O_4$ requires C = 72·13; H = 10·38 per cent.
$C_{11}H_{15}O_2$ „ C = 72·52; H = 9·89 per cent.

These numbers agree better with the formula $C_{22}H_{38}O_4$ than with $C_{11}H_{18}O_2$, but in order to ascertain definitely if the ether were a synthetic product, it was necessary to make a determination of the molecular weight of the substance. Beckmann's boiling-point method was used with ether as solvent, since it was of importance to recover the substance, the quantity at our disposal being very small.

Ether taken = 18·3 grams.

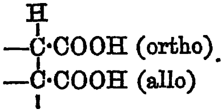
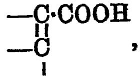
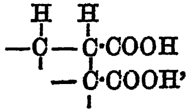
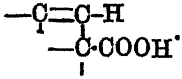
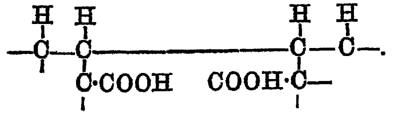
	Weight of substance.	Elevation of b. p.	Mol. weight.
I	0·296	0·103	331
II	0·226	0·072	362

Molecular weight of $C_{22}H_{38}O_4$ = 366.

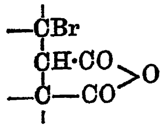
These numbers, together with the fact that bromine is without action on the ether, suffice to show that the substance is the saturated diethylic salt which is normally obtained as a product of electrolysis. The quantity which could be extracted from the tarry residue of high boiling point amounted altogether to little more than a gram, but this is in all probability only a very small proportion of the amount actually formed, the bulk remaining in the tar.

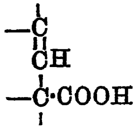
Several attempts were made to saponify the ethereal salt, but they met with little success. The substance is practically unattacked by strong, boiling, alcoholic potash, or by a mixture of concentrated hydrochloric acid and glacial acetic acid. Fuming hydrobromic acid at 160—180° attacks it, but the acid formed has not yet been isolated in sufficient quantity for a study of its properties.

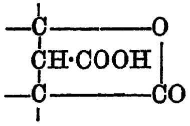
Constitution of Camphoric acid.

As one of us has shown (Trans., 1893, **63**, 506), the electrolysis of sodium ortho-ethylic camphorate and the nature of the products obtained can best be explained by the assumption that camphoric acid contains the complex 
$\begin{array}{l} \;\;\mathrm{H} \\ -\overset{|}{\mathrm{C}}\cdot\mathrm{COOH}\ (\mathrm{ortho}) \\ -\underset{|}{\overset{|}{\mathrm{C}}}\cdot\mathrm{COOH}\ (\mathrm{allo}) \end{array}$. This conclusion is accepted by Noyes, who states that his observations on the behaviour of the camphoramic acids "agree best with the supposition that camphoric acid contains this complex" (*Amer. Chem. J.*, 1894, **16**, 509). Campholytic acid has thus the grouping 
$\begin{array}{l} -\mathrm{C}\cdot\mathrm{COOH} \\ \;\;\| \\ -\underset{|}{\mathrm{C}} \end{array}$, and is an $\alpha\beta$-acid. Allocampholytic acid may be put into the class of $\beta\gamma$-unsaturated acids, on account of the ease with which campholactone may be obtained from it. In its electrolytic formation, the orthocarboxyl group leaves the molecule, together with a hydrogen atom from one of the neighbouring carbon atoms. This hydrogen atom cannot be attached to the allo-carbon atom, for then an $\alpha\beta$-unsaturated acid would be produced. It must, therefore, be attached to a carbon atom in the γ-position relatively to the allo-carbon atom, that is, the molecule of camphoric acid must contain the atomic grouping 
$\begin{array}{l} \;\;\mathrm{H}\quad\mathrm{H} \\ -\underset{|}{\overset{|}{\mathrm{C}}}-\overset{|}{\mathrm{C}}\cdot\mathrm{COOH} \\ \qquad -\underset{|}{\overset{|}{\mathrm{C}}}\cdot\mathrm{COOH} \end{array}$, and allo-campholytic acid the grouping 
$\begin{array}{l} -\underset{|}{\mathrm{C}}{=}\mathrm{C}\text{-}\mathrm{H} \\ \quad -\underset{|}{\overset{|}{\mathrm{C}}}\cdot\mathrm{COOH} \end{array}$. Allo-camphothetic acid would then contain the group 
$\begin{array}{l} \;\;\mathrm{H}\quad\mathrm{H}\qquad\qquad\qquad\qquad\;\mathrm{H}\quad\mathrm{H} \\ -\underset{|}{\overset{|}{\mathrm{C}}}-\overset{|}{\mathrm{C}}-\!-\!-\!-\!-\!-\!-\!-\!-\overset{|}{\mathrm{C}}-\overset{|}{\mathrm{C}}-. \\ \qquad\underset{|}{\overset{|}{\mathrm{C}}}\cdot\mathrm{COOH}\quad\mathrm{COOH}\cdot\underset{|}{\overset{|}{\mathrm{C}}}- \end{array}$

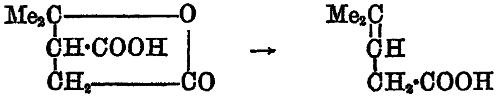
Since lauronolic acid yields the same campholactone as allocampholytic acid, it also must be a $\beta\gamma$-unsaturated acid, and its carboxyl group must occupy the allo-position in the camphoric acid skeleton. The nature of the isomerism of the two acids will probably become clear when further experiments have been undertaken on their reciprocal transformation. Aschan has recently shown that bromocamphoric anhydride, on treatment with alkalis, yields directly a large quantity of lauronolic acid. This, as he points out, indicates that the bromine atom is in the β-position to one of the carboxyl groups, and the simultaneous formation of camphanic acid proves that it is in the γ-position relatively to the other. On our assumption we should have the following groupings

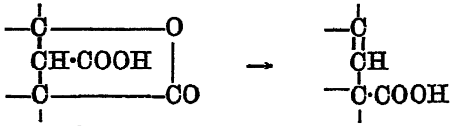

Bromocamphoric anhydride.


Lauronolic acid.


Camphanic acid.

Now camphanic acid, on dry distillation, passes largely into lauronolic acid and carbonic anhydride, just as terebinic acid passes into pyroterebinic acid (compare Bredt, *Ber.*, 1893, **27**, 2098).

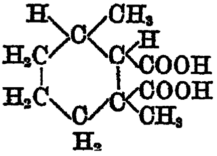

Terebinic acid. Pyroterebinic acid.


Camphanic acid. Lauronolic acid.

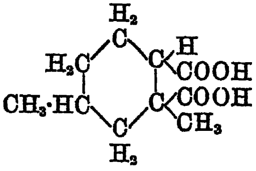
The analogy here is much more perfect than that exhibited when Bredt's formula for camphoric acid is employed, and in the case of Ballo's formula one would expect the lauronolic acid derived directly from bromocamphoric anhydride to be different from that derived from camphanic acid, namely, a βγ-acid in the first instance, and a γδ-acid in the second.

Applying the rules previously found to hold good in electrolysis of alkaline salts of carboxylic acids, Bredt's formula would place both ortho-campholytic and allo-campholytic acids in the γδ-series. Ballo's formula would make them both βγ-acids. But we have found that the two acids undoubtedly belong to different series, namely, ortho-campholytic acid to the αβ-series, and allo-campholytic acid to the βγ-series. This fact seems to us, therefore, a strong argument against the validity of these formulæ. Two formulæ have been proposed, however, which are in harmony with the above exposition, Armstrong's formula (Trans., 1879, **35**, 757) and Collie's formula (*Ber.*, 1892, **25**, 1116). These are

Collie.



Armstrong.



Either of these formulæ explains the results obtained on electrolysis as well as the other, and their further verification must depend on other reactions.

"*Camphothetic*" *acid: a correction.* By J. WALKER.

IN a private communication, Professor Noyes kindly informed me that, by the action of dilute sulphuric acid on campholytic acid, he had obtained a solid isomeride which bore a striking resemblance to the "camphothetic" acid I described in the Transactions (1893, **63**, 504). On reinvestigating my acid, I found that it was an "isocampholytic" acid, $C_9H_{14}O_2$, and not "camphothetic acid," $C_{18}H_{30}O_4$, as I had supposed. The analyses given of the acid and salts agree almost equally well with either formula, and I was led by an error in the molecular weight determination of the ethylic salt, and by the fact that this salt, when perfectly dry, scarcely acts on dry bromine, to attribute to the acid the saturated formula $C_{18}H_{30}O_4$. I find, however, that the ethylic salt immediately decolorises moist bromine in the cold, and that the acid itself when dissolved in dilute sodium carbonate solution at once decolorises a solution of potassium permanganate. A determination of the molecular weight of the ethylic salt by the depression of the freezing point of benzene gave the following results.

Weight of benzene taken = 17·6 grams.

Weight of substance.	Depression.	Mol. weight.
0·372 gram.	0·570	182
0·608 „	0·890	190

The molecular weight of ethylic isocampholytate, $C_{11}H_{18}O_2$, is 182. Thus the acid is doubtless unsaturated, and Professor Noyes informs me, from a direct comparison of his acid with a specimen which I sent him, that "there can be no possible doubt of the complete identity of the two." Beyond the change of formula, no other alteration has to be made at the place cited, except in the dissociation constant, in calculating which the false molecular weight was assumed. The corrected numbers are as follows.

Isocampholytic acid, $C_9H_{14}O_2$.

$$\mu_\infty = 351.$$

v.	μ'.	μ''.	μ.	$100m$.	$100k$.
850	28 6	28·8	28·7	8·18	0·00086

$$K = 0·00086.$$

This constant is not far removed from the constant of the isomeric campholytic acid, K = 0·00093, but is less certain on account of the very slight solubility of the acid. It again exhibits the abnormally small value characteristic of camphor derivatives.

Koenigs and Hoerlin (*Ber.*, 1893, **26**, 813) describe an acid, $C_9H_{14}O_2$, isomeric with campholytic acid, which they obtained by the action of superheated steam on sulphocamphylic acid at 170—190°. As this acid, from their description, exhibited a close similarity in properties to those of isocampholytic acid, it was judged advisable to compare the two substances directly. Mr. Henderson and I, accordingly, prepared a small quantity of isolauronolic acid, following the instructions of Koenigs and Hoerlin, which we can confirm in every particular. The acid obtained was crystallised first from aqueous alcohol, and afterwards from light petroleum. It then melted at precisely the same temperature as isocampholytic acid, namely, 133° (corr.) on an Anschütz normal thermometer. The melting point given by Koenigs and Hoerlin is 135°. The crystals from light petroleum had also in both cases the same crystalline habit, forming small well-defined rectangular tables. The solubility of both acids in water at 25° was identical, one part dissolving in 5000 parts of the solvent. A determination of the dissociation constant of isolauronolic acid gave K = 0·00081, a number almost identical with that given above for isocampholytic acid. The calcium salt is described by them as being easily soluble, and crystallising in needles with approximately 1 mol. of water of crystallisation. This is also the behaviour of the calcium salt of isocampholytic acid. There can thus be little doubt that isocampholytic acid and isolauronolic acid are identical.

As to the real ethylic camphothetate, $C_{22}H_{38}O_4$, it in all probability exists in the highest boiling portion of the electrolysed product; but as it seems to have no tendency to crystallise, like the isomeric ethylic allo-comphothetate, I have not yet been able to isolate it.

With the original product from the electrolysis of sodium orthoethylic camphorate, a comparatively large quantity of camphoric anhydride was obtained on distillation (Trans., 1893, **63**, 498). With another preparation treated in a precisely similar way, not a trace of this or of any other solid substance was found. The products of electrolysis thus seem liable to considerable variation in detail.

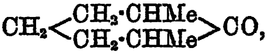
University College, Dundee,
March, 1895.

XLI.—*Dimethylketohexamethylene.*

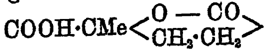
By F. Stanley Kipping, Ph.D., D.Sc.

Some years ago, when engaged in studying the action of phosphoric anhydride on fatty acids (Trans., 1890, **57**, 532 and 980; 1893, **63**, 452), a few experiments were made with various dicarboxylic acids, amongst others *αα'*-dimethylpimelic acid, a compound which happened to be under investigation at the time (Kipping and Mackenzie, Trans., 1891, **59**, 569), and which has formed the subject of a recent communication (this vol., p. 139).

It was then observed that this acid, when heated with phosphoric anhydride, yielded an oil having an odour of peppermint,* but further experiments were necessarily postponed owing to lack of material.

Subsequent researches having necessitated the preparation of a considerable quantity of dimethylpimelic acid for further examination in other directions, the study of its behaviour with phosphoric anhydride was also resumed, but the results were not satisfactory, the yield of the oil in question being very small. Under these circumstances, and as it seemed probable that the product would prove to be dimethylketohexamethylene,  $CH_2<\begin{matrix}CH_2\cdot CHMe\\CH_2\cdot CHMe\end{matrix}>CO$, a different method of preparation was resorted to, and the calcium salt of the acid was submitted to dry distillation, a process which had been previously employed with satisfactory results in the preparation of suberone from suberic acid, and, more recently, in the conversion of several other dicarboxylic acids into cycloid ketones (Semmler, *Ber.*, 1891, **25**, 3517; v. Baeyer, *Ber.*, 1892, **26**, 231; Wislicenus, *Annalen*, 1893, **275**, 309).

In this case, also, the method proved applicable, and the crude dimethylketohexamethylene (Proc., **121**, 68) in the distillate was finally obtained in a state of purity by converting it into the crystalline oxime, and decomposing the latter with hydrochloric acid.

Dimethylketohexamethylene has the strong peppermint-like smell which seems to be characteristic of the saturated cycloid ketones of this class, whereas its oxime has an odour very similar to that of camphoroxime; the general properties of the ketone resemble those of its homologues. On oxidation with nitric acid it is probably first converted into α-methylglutaric acid, $COOH\cdot CHMe\cdot CH_2\cdot CH_2\cdot COOH$; but this compound undergoes further oxidation, yielding αα-hydroxymethylglutaric acid, $COOH\cdot CMe(OH)\cdot CH_2\cdot CH_2\cdot COOH$ (or the lactonic acid  $COOH\cdot CMe{<}\substack{O-CO\\ CH_2\cdot CH_2}{>}$), just as β-methyladipic acid, $COOH\cdot CH_2\cdot CHMe\cdot CH_2\cdot CH_2\cdot COOH$, is converted into ββ-hydroxymethyladipic acid, $COOH\cdot CH_2\cdot CMe(OH)\cdot CH_2\cdot CH_2\cdot COOH$ (or the lactonic acid $COOH\cdot CH_2\cdot CMe{<}\substack{O-CO\\ CH_2\cdot CH_2}{>}$), on oxidation with potassium permanganate (Semmler, *loc. cit.*).

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* Not an odour of turpentine as originally stated (Kipping and Mackenzie, *loc. cit.*); a reference to the author's note-book has shown that this misstatement arose in writing the paper, as in the notes of the experiment the oil is described as having "a strong odour of peppermint."

Preparation of Crude Dimethylketohexamethylene.

The material employed in these experiments consisted of a sample of liquid dimethylpimelic acid, which had been purified by distillation under reduced pressure, and from which, after keeping for several months, the crystalline acid had been separated by filtration; this liquid, therefore, was probably a mixture of the two stereoisomeric modifications of the acid, free from any appreciable quantity of impurity (compare this vol., p. 139).

The calcium salt was prepared by dissolving the liquid acid in hot water, adding excess of precipitated calcium carbonate to the boiling solution, and filtering; on evaporation, the filtrate yielded the readily soluble salt in the form of a pasty mass, which was first heated at about 120° until it became hard and brittle, and then intimately mixed with an equal weight of dry, powdered, soda-lime. This mixture, in quantities of about 8 grams, was then submitted to dry distillation in small, hard-glass retorts, under a pressure of about 400 mm.; at first, it became pasty and frothed up, but, on continued heating, an oil began to collect in the receiver, and the residue in the retort gradually changed to a hard, grey mass. The dark brown and slightly fluorescent, oily distillate was dissolved in ether, the solution shaken with dilute potassium carbonate, dried over anhydrous potassium carbonate, filtered, and evaporated; the weight of the residue, when practically free from ether, amounted to about 40 per cent. of that of the calcium salt employed.

When distilled under ordinary pressure, the oil began to boil at about 150°, but the temperature rapidly rose to 165°, and the principal portion of the product passed over between 165° and 185°; above this, only a small quantity was collected, and, although the thermometer subsequently rose to 250°, a thick, brown oil still remained in the distilling flask. The fraction 165—185° was now redistilled and collected in two principal portions, boiling at 170—175° and 175—179° respectively; both of these were almost colourless, and had a strong odour of peppermint.

An analysis of the fraction boiling at 175—179°, which was the larger of the two, gave results agreeing well with those required by dimethylketohexamethylene.

0·1737 gave 0·4876 CO_2 and 0·1733 H_2O. C = 76·5; H = 11·1.
$C_8H_{14}O$ requires C = 76·2; H = 11·1 per cent.

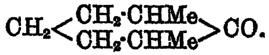
Dimethylketohexamethylene Oxime.

In order to obtain the ketone in a state of purity, without the unavoidable loss which would have attended further fractional distillation, the two portions just referred to were dissolved in methylic alcohol, and the solution mixed with a slight excess of hydroxylamine hydrochloride in aqueous solution and about four times the theoretical quantity of concentrated soda; after warming gently for a short time, this mixture was left to evaporate at the ordinary temperature. The oxime, which was slowly deposited in colourless crystals, was separated by filtration, washed with water, and spread on porous earthenware to free it from oil; it was then recrystallised from hot dilute alcohol, dried over sulphuric acid, and analysed.

0·1387 gave 0·3460 CO_2 and 0·1344 H_2O. C = 68·03; H = 10·76.
$C_8H_{14}\!:\!NOH$ requires C = 68·08; H = 10·64 per cent.

Dimethylketohexamethylene oxime crystallises from warm dilute alcohol and from other solvents in long, colourless prisms, melting at 114—115°; it dissolves freely in cold acetone, ether, and chloroform, but is only moderately easily soluble in cold alcohol, and insoluble, or nearly so, in water and also in concentrated soda; on the other hand, it is readily soluble in warm, moderately strong hydrochloric acid, by which it is decomposed (see below). The oxime has a very peculiar and somewhat unpleasant smell, very like that of camphor oxime; it is volatile in steam, and distils under ordinary atmospheric pressure without visibly decomposing if heated in small quantities at a time. Crystals of the oxime suitable for goniometrical measurement were not obtained; those deposited from alcoholic solution belonged apparently to the anorthic system.

Dimethylketohexamethylene,



$$CH_2<\begin{matrix}CH_2\cdot CHMe\\CH_2\cdot CHMe\end{matrix}>CO.$$

As the oxime can be easily obtained in a state of purity, and is readily reconverted into the ketone by the action of hydrochloric acid, it afforded a convenient means of preparing pure dimethylketohexamethylene. For this purpose, the crystalline compound was gently warmed with moderately concentrated hydrochloric acid, in which, at first, it rapidly dissolved; in a very short time, however, the solution became turbid, owing to the separation of a colourless oil, and, on distilling in a current of steam, the ketone quickly passed over. The distillate was extracted with ether, the ethereal extract dried over calcium chloride, and evaporated; on distilling the residual oil under atmospheric pressure, the thermometer rose at once to 174°, and practically the whole of the ketone passed over at 174—176°, only a few drops remaining in the distilling flask.

This preparation, therefore, consisted of pure dimethylketohexamethylene, and, as analyses of the oxime and of the less pure ketone had already established its composition, another combustion was deemed superfluous.

Dimethylketohexamethylene is a colourless, mobile liquid, specifically lighter than water at 16°, and readily volatile in steam; it has a very strong and pure odour of peppermint. It is practically insoluble in water, but is miscible with alcohol, ether, and other organic liquids in all proportions; its melting point is doubtless very low, as it showed no signs of crystallising when cooled to 0°. Attempts to prepare a crystalline additive compound by shaking the ketone with a strong solution of sodium hydrogen sulphite were unsuccessful; on the other hand, it was readily acted on by phenylhydrazine in warm acetic acid solution, giving a yellowish, oily hydrazone.

Although there could be little doubt, considering its method of formation and its general properties, that this ketone has the constitution assigned to it above, its behaviour on oxidation was investigated in the hope of obtaining confirmatory evidence of this view. The pure ketone, prepared from the oxime, was therefore slowly added to a considerable quantity of warm nitric acid of sp. gr. 1·2, whereupon a vigorous action occurred, showing that, like ketopentamethylene (W. Hentzschel and Wislicenus, *Annalen*, 1893, **275**, 312), the compound was very readily oxidised. As, however, the oil did not readily pass into solution, and brown fumes continued to be evolved even after warming for some time, the mixture was heated on a sand bath until oxidation appeared to be at an end; on then evaporating to a syrup and adding a little water, a very small quantity of a crystalline substance (see below) was deposited, but after separating this by filtration and again evaporating, the bulk of the oxidation product remained as a colourless syrup. As this syrup did not solidify even when, after keeping for some days over sulphuric acid, it was rubbed with a crystal of α-methylglutaric acid—an acid which might well have been obtained as an oxidation product of the ketone—it appeared probable that oxidation had proceeded beyond this stage and that the α-methylglutaric acid, which it may be assumed had been produced in the first instance, had been partially converted into $\alpha\alpha$-hydroxymethylglutaric acid, in the same way as the β-methyladipic acid obtained by Semmler as an oxidation product of methylketopentamethylene may be transformed into ββ-hydroxymethyladipic acid (*Ber*., 1892, **25**, 3513). For this reason the syrup was again heated with concentrated nitric acid, as it seemed probable that further oxidation would lead to a more homogeneous, and possibly crystalline product. This supposition proved to be well founded, since, on again evaporating until free from nitric acid and then keeping the residual syrup over sulphuric acid, it was slowly converted into a colourless, crystalline mass, which was freed from adherent oil with the aid of porous earthenware. When purified in this way, the compound melted, not very sharply, at 65—68°, had an acid reaction, and dissolved in cold sodium carbonate solution with effervescence; it charred when distilled under ordinary atmospheric pressure, giving an oily distillate which soon solidified and which, as far as could be ascertained, was identical with the original substance. As the oxidation product was so very readily soluble in water, alcohol, ether, &c., the small quantity at disposal could not be purified by recrystallisation, and, partly for this reason, it was not analysed. There is little doubt, however, judging from its method of preparation and properties, that it is the lactone of αα-hydroxymethylglutaric acid and identical with the compound described by Bredt (*Annalen*, 1881, **208**, 62; *Ber*., 1881, **14**, 1780) and by Kreckeler, Tollens and Block (*Annalen*, 1887, **238**, 287).

This view was confirmed by an analysis of the silver salt; a portion of the acid was dissolved in dilute ammonia and the neutral solution precipitated with silver nitrate; the precipitate was collected with the aid of the pump, and dried first on porous earthenware over sulphuric acid, and finally at 100°, at which temperature it did not appreciably darken.

0·3111 gave 0·2176 CO_2, 0·0659 H_2O and 0·1796 Ag. C = 19·0; H = 2·4; Ag = 57·6 per cent.

$C_6H_8O_5Ag_2$ requires C = 19·2; H = 2·1; Ag = 57·4 per cent.

This result, as will be seen, agrees well with that required for the silver salt of a hydroxymethylglutaric acid, and the properties of the salt were the same as those of the compound described by Bredt; it was very sparingly soluble in water, and appeared to be amorphous when examined under the microscope.

The crystalline oxidation product of the ketone, referred to above, proved to be a mixture, as, on recrystallising it from dilute alcohol, very long flat plates or needles and small compact crystals were deposited side by side; these two compounds were separated, partly mechanically, partly by fractional crystallisation, and eventually obtained in a state of purity, but in quantities so small that analyses were out of the question.

The long, flat plates melted at 113—114°, and probably belonged to the anorthic system; they were at first thought to be crystals of methylsuccinic acid, the melting point of which is 112°; they were, however, insoluble in water, or nearly so, whereas methylsuccinic acid is readily soluble.

The other crystalline oxidation product melted at 108—109° and was also insoluble, or nearly so, in water; it formed orthorhombic octahedra, and was therefore not identical with the substance melting at 113—114°.

Unfortunately the nature of these two acids remained undetermined, owing to the very small quantities which were produced; as, however, the ketone which was submitted to oxidation must have been of a high degree of purity, having been prepared from the pure oxime, these products can hardly have been derived from any extraneous source, and their formation is therefore of some interest.

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XLII.—*Sulphonic Derivatives of Camphor.* Part II.

By F. Stanley Kipping, Ph.D., D.Sc., and W. J. Pope.

During the combustion of bromocamphorsulphonic chloride and of the other sulphonic derivatives of camphor which have been recently described by us (*Trans.*, 1893, **63**, 548), it was noticed that a rapid effervescence set in almost as soon as the substance had melted, but that very little charring occurred until some time afterwards. These observations led us to examine the nature of this decomposition, and it was found that the effervescence was due to the evolution of sulphurous anhydride, the sulphonic chlorides being thus converted into halogen derivatives of camphor.

Although this behaviour is not characteristic of sulphonic derivatives of camphor, as we first thought it to be, a similar change having in fact been observed in the case of benzylsulphonic chloride, $C_6H_5 \cdot CH_2 \cdot SO_2Cl$ (Pechmann, *Ber.*, 1873, **6**, 534), and in other instances, it seemed desirable to make a study of the halogen derivatives obtained in this way and to compare them with the known halogen derivatives of camphor.

For this purpose, however, it was first necessary to improve the methods of preparing the sulphonic chlorides, especially of the camphorsulphonic chlorides, which had hitherto been obtained only by a very troublesome process. In most cases, this object was accomplished by making a comparatively small alteration in the method previously used, the solution of the crude calcium salt of the sulphonic acid being treated with ammonium carbonate instead of with sodium carbonate, as it had been found that the ammonium sulphonates invariably crystallised far more readily than the sodium salts, and were consequently much more easily purified. The ammonium salts have a further advantage over the sodium salts in that they are anhydrous; the prolonged heating which was required in order to dehydrate the latter salts, and which appeared to lead to partial decomposition, thus became unnecessary. By proceeding in this way we obtained much less impure products for treatment with phosphorus pentachloride and the yields of the sulphonic chlorides were very materially increased, so that we were able to prepare the derivatives of bromocamphor and chlorocamphor and optically inactive camphorsulphonic chloride in large quantities. Optically active camphorsulphonic chloride, of which we had previously succeeded in obtaining only a few grams, also became an easily accessible substance, as it was found that the ammonium salt of active camphorsulphonic acid could be prepared in almost any quantities by reducing the corresponding salt of bromocamphorsulphonic acid with zinc dust and ammonia.

As it appeared probable that the sulphonic bromides corresponding with the above-mentioned chlorides, would undergo decomposition when heated, and give rise to new bromo-derivatives of camphor, we also prepared these compounds by treating the ammonium salts of the respective acids with phosphorus pentabromide. In all cases these sulphonic bromides were easily separated in a state of purity, and were readily converted into the desired bromo-derivatives of camphor.

The following is a list of the sulphonic derivatives of camphor which have now been investigated, those marked with an asterisk having been described in our first communication.

*Dextro-rotatory camphorsulphonic chloride, $C_{10}H_{15}O\cdot SO_2Cl$.
*Inactive camphorsulphonic chloride, $C_{10}H_{15}O\cdot SO_2Cl$.
Dextro-rotatory camphorsulphonic bromide, $C_{10}H_{15}O\cdot SO_2Br$.
Inactive camphorsulphonic bromide, $C_{10}H_{15}O\cdot SO_2Br$.
*Bromocamphorsulphonic chloride, $C_{10}H_{14}BrO\cdot SO_2Cl$.
Bromocamphorsulphonic bromide, $C_{10}H_{14}BrO\cdot SO_2Br$.
*Chlorocamphorsulphonic chloride, $C_{10}H_{14}ClO\cdot SO_2Cl$.
Chlorocamphorsulphonic bromide, $C_{10}H_{14}ClO\cdot SO_2Br$.

The sulphonic bromides, like the sulphonic chlorides previously described, are compounds of great beauty, and, with the exception perhaps of chlorocamphorsulphonic bromide, are readily obtained in massive colourless crystals; we were unable, however, to obtain well-defined individual crystals of the latter substance, and also of the corresponding bromocamphorsulphonic bromide, so that their crystallographic description is not so complete as might be desired. Bromocamphorsulphonic bromide seems to be crystallographically dissimilar from the corresponding bromosulphonic chloride; the crystallographic relationship between the dextrorotatory camphorsulphonic chloride and bromide is, however, a very close one. The two oppositely active modifications of camphorsulphonic bromide, like those of the corresponding sulphonic chloride, do *not form* a very definite racemic modification, so that on allowing a solution of the synthetic mixture to evaporate, both right- and left-handed enantiomorphous crystals are sometimes deposited side by side.

The chemical behaviour of the sulphonic bromides has not yet been examined in any detail except as regards their conversion into halogen derivatives of camphor under the influence of heat; in this respect, it is interesting to note that they are much more readily decomposed than the sulphonic chlorides, and yield, in all cases, approximately the theoretical quantity of the pure halogen derivatives, whereas the sulphonic chlorides usually give a considerable quantity of carbonaceous matter and in some cases also a mixture of crystalline products. The numerous halogen compounds which have been obtained by the decomposition of these sulphonic derivatives will be described in our next paper.

Preparation of Bromo- and Chloro-camphorsulphonic Chlorides.

For the sulphonation of bromocamphor we now employ chlorosulphonic acid, and have, for the present, entirely given up the use of anhydrosulphuric acid (*loc. cit.*, p. 576) in this and in other cases on account of the trouble of afterwards separating the large excess of sulphuric acid which has to be employed.

The improved method of preparing bromocamphorsulphonic chloride is carried out as follows:—Bromocamphor (100 grams) is dissolved in chloroform (200 grams), freshly-distilled chlorosulphonic acid (75 grams = $1\frac{1}{2}$ mols.) added, and the solution heated on a water bath for about 12 hours; when cold, the whole is poured into water, the chloroform separated, and the aqueous solution neutralised with chalk. After separating the calcium sulphate, the hot solution of the calcium bromocamphorsulphonate is mixed with the requisite quantity of ammonium carbonate, and the precipitated calcium carbonate got rid of by filtration. The pale brown filtrate is then evaporated until, on cooling, it gives a thick paste of fine needles, which is filtered from the solution of ammonium chloride and washed with methylated spirit. The product is an almost colourless, felted mass of crystals, and, after once recrystallising from boiling water, is allowed to dry in the air; the yield of practically pure ammonium salt is about 125 grams from 100 grams of bromocamphor.

In converting the ammonium bromocamphorsulphonate into the sulphonic chloride, the dry salt, in quantities of about 50 grams, is triturated with rather more than the theoretical quantity of phosphorus pentachloride, action being started, if necessary, with the aid of a drop of phosphorus oxychloride, and the pentachloride being added gradually, so that the operation occupies about half an hour. The oily product, isolated by extracting with chloroform as previously described (*loc. cit.*, p. 581), solidifies on cooling to a mass of crystals, and is very much less impure than the preparation obtained by the earlier process; when washed with a little ether on the pump, it yields a snow-white powder which consists of practically pure bromocamphorsulphonic chloride; 100 grams of the ammonium salt give, on the average, about 90 grams of the sulphonic chloride.

The preparation of chlorocamphorsulphonic chloride is carried out in an exactly similar manner; the yield of practically pure ammonium chlorocamphorsulphonate is about 130 grams from 100 grams of chlorocamphor, and 100 grams of this salt give about 80 grams of crystalline sulphonic chloride.

Preparation of Optically Inactive Camphorsulphonic Chloride.

In preparing this substance, we proceed as described in our first paper, but instead of neutralising the aqueous solution of the product of sulphonation with barium carbonate (*loc. cit.*, p. 553), we now use calcium carbonate, and then convert the calcium camphorsulphonate into the ammonium salt in the manner detailed above. The solution of the ammonium salt is concentrated as far as possible over a naked flame, and then heated for some days on the water bath; the residual syrup does not crystallise very readily, but when kept for some time it slowly changes into a crystalline sludge, which is collected with the aid of the pump; the residue is then recrystallised from a little methylated spirit and dried in the air. This preparation still contains a little ammonium chloride, which may be got rid of by recrystallising from water; this step, however, is unnecessary when the salt is to be used for the preparation of the sulphonic chloride.

The treatment of the ammonium salt with phosphorus pentachloride having been carried out in the usual manner (using about 36 grams to every 50 grams of the salt), and the product extracted by shaking with chloroform, the crude sulphonic chloride is obtained as a thick, yellow oil, the yield of which is usually about 65 per cent. of the ammonium salt taken. This oil does not crystallise very readily or completely even when kept several days, and for this reason the most rapid method of purifying it is to extract the crude product with light petroleum as previously described (*loc. cit.*, p 551); the crystalline deposits from the various extracts are then recrystallised from ethylic acetate.

The purified product contains in this case, as before, a slight excess of dextrorotatory camphorsulphonic chloride (*loc. cit.*, pp. 554—556), which may be separated to some extent by fractional crystallisation; the remaining portions consist of approximately inactive camphorsulphonic chloride having the peculiar properties already described.

The light petroleum solutions from which the camphorsulphonic chloride is separated contain two more readily soluble bye-products, an account of which will form the subject of a later paper.

Preparation of Dextrorotatory Camphorsulphonic Chloride.

Dextrorotatory camphorsulphonic chloride was first obtained during the purification of the mixture of optically active sulphonic chlorides, produced by treating the crude sodium camphorsulphonate with phosphorus pentachloride (*loc. cit.*, p. 554); its extraction, however, was such a tedious operation, and such very small quantities were obtained, that its investigation was necessarily limited. We were therefore led to attempt its preparation in other ways, and for this purpose we studied the action of reducing agents on ammonium bromocamphorsulphonate, a compound which could easily be obtained in large quantities. The following method for the preparation of the active camphorsulphonic chloride was finally adopted:—Ammonium bromocamphorsulphonate (100 grams) is dissolved in dilute ammonia, and zinc dust added in small quantities at a time; a very considerable rise of temperature occurs at first, but after a time the action slackens, and fresh additions of zinc dust produce no effect; after heating on a water bath for about half an hour, the solution is filtered, the filtrate saturated with hydrogen sulphide, and the zinc sulphide separated. On evaporating the solution to dryness, an almost colourless mass of crude dextrorotatory ammonium camphorsulphonate, containing, however, a considerable quantity of ammonium bromide, is obtained; this mixture. when dried in the air, is employed, without further purification, for the preparation of the sulphonic chloride, the quantity of phosphorus pentachloride which is used being rather more than that calculated on the assumption that the salt is a mixture of ammonium camphorsulphonate and ammonium bromide in molecular proportion. The treatment with the pentachloride and the extraction of the sulphonic chloride with chloroform are carried out in the usual manner.

The crude product is a pale, yellowish-green oil which soon begins to crystallise; after keeping it several days over sulphuric acid, it is mixed with a little dry ether, and the solid collected and recrystallised from ethylic acetate. The compound thus obtained crystallises in beautiful, well-defined, transparent tetrahedra melting at 137·5°; its identity with the optically active camphorsulphonic chloride described in our earlier paper was fully established by an examination of the ordinary properties of the substance as well as by a series of crystallographic measurements.

Optically Inactive Camphorsulphonic Bromide, $C_{10}H_{15}O{\cdot}SO_2Br$.

The crude ammonium salt obtained from the product of the sulphonation of camphor with chlorosulphonic acid (p. 357), consists of a mixture of the dextro- and lævo-rotatory ammonium camphorsulphonates with a little ammonium chloride; for the preparation of optically inactive camphorsulphonic bromide, this salt is triturated with rather more than the theoretical quantity of phosphorus pentabromide, and, after an interval of about an hour, the brown, homogeneous, oily liquid is well mixed with powdered ice; the sulphonic bromide, which separates as a yellow oil, is extracted with chloroform, the washed extract dried with calcium chloride, and the solvent evaporated on the water bath. The yellow, oily residue slowly solidifies, and, after washing with a little ether, the colourless crystalline product consists of practically pure camphorsulphonic bromide; the yield is about 35 per cent. of the crude ammonium salt.

Although we call this preparation optically inactive camphorsulphonic bromide for the sake of convenience, it may be stated at the outset that it is very doubtful whether the two optically active modifications unite to form a definite racemic compound; the whole behaviour of the substance is, in fact, very similar to that of the mixture of optically active camphorsulphonic chlorides (*loc. cit.*, p. 560), as will be seen from the following description of its properties.

On recrystallising the preparation from ethylic acetate, it is usually deposited in the first place in large, thin, transparent plates, aggregated together so as to form a honeycomb-like mass. These crystals melt, but not at all sharply, at about 125—128°, and their formation seems to be associated with the presence of excess of one of the optically active modifications, as they are usually met with only during the first separations. They first begin to form at the surface of the solution as regularly branched dendritic growths which, during the cooling, move rapidly about on the surface; the skeletal outlines of the crystals subsequently become filled in, and they are ultimately obtained as poorly-developed, very transparent, quadratic plates, which have straight extinction, and show the biaxial interference figure characteristic of the butterfly-like crystals described below. The sides of the plates are at about 90° to each other, and on examining the thinner crystals in a parallel beam of polarised light, the differences in the interference colours in different parts of the plate reveal the presence of small included crystals, which most frequently have a triangular shape. From the indefinite melting point, and from the crystallographic examination of these plates, it must be concluded that they represent a heterogeneous mixture of the two optical antipodes.

After separating the plates just described, and allowing the filtrate to evaporate spontaneously, crystals of various kinds are deposited; as a rule, large, transparent, prismatic masses of somewhat irregular shape are deposited, together with smaller, apparently well-defined prisms, similar in appearance to those of the optically inactive camphorsulphonic chloride (*loc. cit.*, p. 561); like the latter, moreover, these prisms have no definite melting point, but sinter together towards 115—120°, and frequently do not melt completely until the temperature rises to about 138°, effervescence then taking place; they evidently consist of a heterogeneous mixture of the two optically active modifications, different parts of one and the same apparently simple crystal sintering and melting at different temperatures; if also part of an apparently homogeneous crystal be crushed to a fine powder, the latter usually sinters at 115—120°, whereas the rest of the crystal often does not undergo any visible change at this temperature.

Although apparently so well defined, these prisms are in reality so poorly developed that measurements were impossible. They seem, however, to be orthorhombic, showing the forms $m\{110\}$ and $o\{111\}$, with traces of the pinacoids $a\{100\}$ and $b\{010\}$, but the forms may with equal probability be $a\{100\}$, $b\{010\}$, $d\{101\}$, $d'\{011\}$, with traces of the prism $m\{110\}$. An attempt to measure one of the best developed of these crystals showed that the angle $110:\bar{1}10$, or $100:010$, is approximately 90°; if, therefore, as is possible, these prisms consist essentially of approximately equal-sized hemihedral crystals of the dextro- and lævo-modifications, twinned together to form an apparently holohedral, though badly defined, individual, it is obvious that fairly exact measurements would be required in order to decide which of the two sets of indices given above be the correct one; for from these measurements it would have to be decided which was the angle $110:\bar{1}10$, and which the angle $100:010$, and since the latter is 90°, and the former—from the approximate equality of the *a*- and *b*-axes—is very nearly 90°, this would be a matter of considerable difficulty.

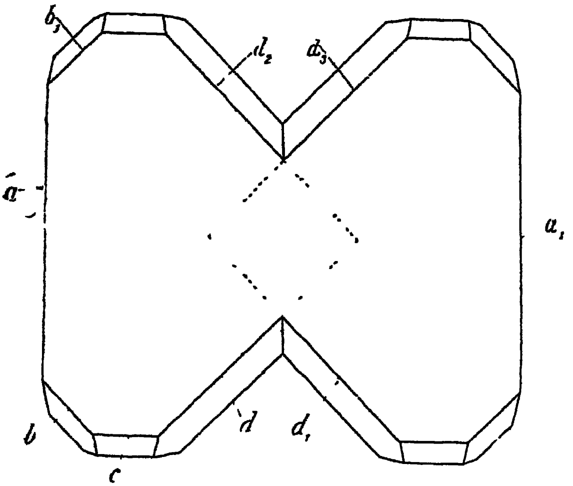
The extinction through the faces in the prism zone is straight, but no trace of an interference figure could be seen through these faces in convergent polarised light; on chipping fragments from one of these crystals, a piece was found through which could be seen a biaxial interference figure of about the same angle as that observed through the butterfly-shaped crystals described below. The orientation of the fragment was apparently such that its faces lay approximately in the prism zone, so that if this were so, the acute bisectrix was perpendicular to the zone axis. The crystals have no distinct cleavage, the fracture is highly conchoidal, and the double refraction is moderately strong and positive in sign.

In our preceding communication, we described prismatic crystals of optically inactive camphorsulphonic chloride, which exhibited the forms *m*{110}, *o*{111}, and more rarely *b*{010}; these forms occupy the same relative positions on the crystal as those present on the prismatic crystals of the corresponding sulphonic bromide; the general appearance of the prisms of the two substances is also very similar, although those of the sulphonic bromide are much more ill-defined than those of the sulphonic chloride. The close resemblance between these two sets of crystals, both in optical and geometrical properties, renders it extremely probable that they are crystallographically similar; it must, therefore, be concluded that the prismatic crystals of optically inactive camphorsulphonic bromide, like those of the sulphonic chloride, consist of a heterogeneous mixture of the two optically active substances, which possess but little tendency to form a true racemic modification.

Side by side with the prisms, curiously shaped, butterfly-like. transparent plates are sometimes deposited; these crystals also have no definite melting point, and, like the plates and prisms, they appear to be heterogeneous mixtures; portions chipped from the corners of the triangular pieces melt fairly sharply at about 127°, but when a whole crystal is crushed to a powder, the latter melts at 115—125°.

These butterfly-shaped crystals (fig. 1, p. 362) are seen to consist each of two individuals, one of which is usually rather thicker than the other, although both lie in the same plane; on microscopic examination under a low power, it is seen that the two modified triangular parts interpenetrate, as the edges *d* can be traced in both individuals as shown by the dotted lines in the figure; the plane angle *ac*, as measured on the microscope stage, is 90°, the plane angle *ab* is 140°, and the plane angle *ad* is 45°. In parallel polarised light, the thin crystals are seen to include much smaller ones, which are usually triangular in outline; the latter, in all probability, consist of partially developed tetrahedra of the pure optically active modifications; the extinction in the mass of the twin crystals is parallel to the edge *a*. In convergent polarised light, under a $\frac{1}{12}$th oil immersion objective,

FIG. 1.



the trace of the optic axial plane is found to be perpendicular to the *a*-edges, and the upper surface of the crystal is perpendicular to the acute bisectrix of both halves of the twin. The interference figure is a normal orthorhombic one, and the optic axial angle for red is greater than that for blue; the angle in air for yellow sodium light was measured in glycerol in the axial angle apparatus, and found to be 37° 30′ as the mean of measurements on four different crystals. The double refraction is positive and moderately strong and the dispersion is small; no definite cleavage could be distinguished, and the fracture is conchoïdal. Since the upper surface of the crystals is perpendicular to a bisectrix and the extinction is parallel to *a*, the forms present would seem to be {100}, {010}, {101}, and {111}; if the two wings of the twin are hemihedrally developed, the two halves of the latter form {111} are present. It cannot, however, be stated with certainty that the wings of the crystals are hemihedral, although their unsymmetrical development seems very distinctly to point to this conclusion.

There are, in fact, two ways of regarding these crystals; it may be supposed either that they consist of two crystals of a racemic modification, which have grown in juxtaposition, or that they consist of partially interpenetrant twins made up of two individual crystals, one of dextrorotatory, the other of lævorotatory camphorsulphonic bromide. The first supposition is extremely improbable because of the unsymmetrical development of the crystals, which would not be expected in an inactive or racemic compound, and because of the improbability of two unsymmetrical crystals of the same substance growing in juxtaposition in a symmetrical manner so as to increase the symmetry of the whole. The alternative, that these crystals consist of partially interpenetrant twins of two crystals of oppositely active forms, seems, on the whole, the more probable on crystallographical grounds; in order, therefore, to account for the fact that a portion of one of the wings has not the same melting point (144—145°) as the pure optically active modifications, it is only necessary to make the further very probable assumption that the included tetrahedra, which are visible imbedded in the wings, are those of both the active forms and not of the corresponding modification only.

Finally, in addition to the various forms already described, well-defined tetrahedra of the pure optically active camphorsulphonic bromide are deposited from the ethylic acetate solution under certain conditions; these crystals are easily recognised by their characteristic appearance, and are fully described later.

That all these different crystals, except the tetrahedra, really consist of a mixture of the two oppositely active modifications of camphorsulphonic bromide, was proved by repeatedly recrystallising a sample of the well-defined prisms from ethylic acetate; in some cases, the four-sided plates were deposited, in others the butterfly-shaped crystals, in others the prisms; frequently the two latter were deposited side by side; it was thus shown that the various forms represent one and the same substance.

The original preparation of the inactive substance invariably contains a slight excess of the dextrorotatory modification, and for this reason its solution has a feeble action on polarised light; in one case, for example, the whole of a preparation weighing about 10 grams was separated by crystallisation into three fractions, which, on examination in the polarimeter, were found to have a specific rotation $[\alpha]_D = +3\cdot98°$, $8\cdot30°$, and $13\cdot59°$ respectively; the excess of the dextrorotatory form in the original sample amounted, in fact, to about 6 per cent., the specific rotation of the pure optically active compound being $[\alpha]_D = +145°$.

By repeated fractional crystallisation it is possible to separate most of this excess and to obtain samples which are only very feebly optically active; such samples show the same curious behaviour as that exhibited by similar preparations of camphorsulphonic chloride (*loc. cit.*, p. 563), that is to say, when they are slowly recrystallised from ethylic acetate, well-defined tetrahedra of *both* the optically active modifications are sometimes deposited side by side. A sample, consisting only of well-defined prisms, was repeatedly recrystallised, but without separating any portion of the substance; after several unsuccessful attempts, in which prisms, &c., were deposited, a considerable portion of the substance separated in the characteristic tetrahedra of the optically active forms; these were not all of the same kind, because when heated singly they invariably melted almost sharply at 144—145°, whereas the powder obtained by crushing together a number of the well-defined crystals sintered at temperatures ranging from 130° to 135° in different cases, and melted completely below 140°; a perfectly homogeneous mixture of several tetrahedra would, doubtless, have melted at an even lower temperature, but such a mixture could not be prepared by fusing the crystals together, owing to the low temperature at which the mixture begins to decompose. On re-dissolving a number of these same tetrahedra in ethylic acetate and then allowing the solution to evaporate, the transparent prisms were again obtained.

It is clear, therefore, that, from one and the same solution, the two active modifications may be deposited side by side, or they may crystallise together in indefinite proportions, a behaviour which confirms our previous observations with optically inactive camphorsulphonic chloride.

As regards the other properties of the inactive sulphonic bromide, it may be mentioned that the substance crystallises very readily; it dissolves freely in chloroform, benzene, and ethylic acetate, but is less readily soluble in ether, and only sparingly in boiling light petroleum. When heated at about 145°, it is rapidly decomposed with evolution of sulphurous anhydride, yielding an optically inactive bromocamphor, which will be described in our next paper.

Dextrorotatory Camphorsulphonic Bromide, $C_{10}H_{15}O{\cdot}SO_2Br$.

This is easily prepared from the mixture of dextrorotatory ammonium camphorsulphonate and ammonium bromide, which is obtained by reducing ammonium bromocamphorsulphonate with zinc dust and ammonia in the manner already described (p. 358). The air-dried salt is triturated with a slight excess of the quantity of phosphorus pentabromide, calculated on the assumption that the salt is a mixture of ammonium camphorsulphonate and ammonium bromide in molecular proportion, and, after some time, the pasty mass is stirred into ice; the sulphonic bromide, which separates in a partially solid condition, is then isolated by extracting with chloroform; the yield is good. The crude product soon begins to crystallise, and, after keeping for a few days, it is washed with ether and finally recrystallised from ethylic acetate, from which it is usually deposited at ordinary temperatures in beautiful, lustrous tetrahedra or octahedra (Figs. 2 and 3).

Dextrorotatory camphorsulphonic bromide decomposes and melts at 144—145° almost sharply; although whole tetrahedras become opaque some time before they melt, they do not seem to decompose to any appreciable extent below 144°, provided they are heated very quickly from about 130°. If, however. the crystals be crushed to a fine powder and then heated very slowly, decomposition sets in below 140° and the substance gradually liquefies. The behaviour of the active sulphonic bromide towards solvents is much the same as that of the inactive compound; it dissolves freely in chloroform and ethylic acetate, but is less readily soluble in ether, and only sparingly so in boiling light petroleum; it is only very slowly hydrolysed by boiling with water, but rapidly by hot potash.

FIG. 2.

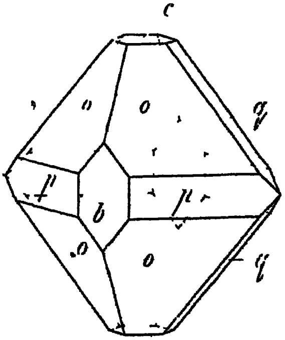
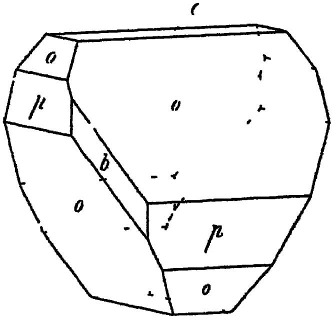


FIG 3



The specific rotation of this compound was found to be $[\alpha]_D = +145°$. 1·8820 grams were dissolved in chloroform, the solution made up to 25 c.c., and examined at 12° in a 2-dm. tube; $[\alpha]_D = +21° 50'$ as the average of eight concordant observations.

The tetrahedra or octahedra which are deposited from a cold ethylic acetate solution of the sulphonic bromide are frequently a centimetre or so in diameter; the tetrahedral crystals closely resemble those of dextrorotatory camphorsulphonic chloride, but may be distinguished from them by their greater lustre. Both the tetrahedra and the octahedra have the same crystallographic dimensions, and can be obtained showing the same forms; the form *o*, $\kappa\{111\}$ is the largest present on the tetrahedra, whilst on the octahedra both this and the other semi-form *o*, $\kappa\{1\bar{1}1\}$ are of approximately the same size; these two forms give only moderately good reflections. The pinacoids $a\{100\}$, $b\{010\}$, and $c\{001\}$ are very small, and the latter only is usually present; these forms are brilliant, and their faces give good, though faint, reflections. The remaining forms $p\{110\}$, $q\{101\}$, and $r\{011\}$ are but rarely present, and occur simply as narrow strips which are only moderately bright.

Crystalline System—Orthorhombic. Sphenoidal hemihedrism.

$$a : b : c = 0{\cdot}9816 : 1 : 1{\cdot}0249.$$

Forms observed:

a .... $\{100\}$......$\infty\breve{P}\infty$

b .... $\{010\}$......$\infty\bar{P}\infty$

c .... $\{001\}$......oP.

o .... $\kappa\{111\}$...... $+$P.

o'.......... $\kappa\{1\bar{1}1\}$...... $-$P.

p .... $\{110\}$......∞P.

q .... $\{101\}$......$\breve{P}\infty$.

r .... $\{011\}$......$\bar{P}\infty$.

The following angular measurements were obtained:—

Angle.	No of observations.	Limits.	Mean.	Calculated.
$bo = 111 : 010$	28	54° 26′— 54° 47′	54° 40′	—
$oq = 111 : 101$	34	34 45 — 35 50	35 20	35° 20
$oo' = 111 : 1\bar{1}1$	8	70 28 — 70 52	70 39	70 40
$oo' = 111 : \bar{1}1\bar{1}$	4	109 1 —109 34	109 17	109 20
$oc = 111 : 001$	19	55 15 — 56 19	55 39	—
$op = 111 : 110$	12	34 9 — 35 1	34 25	34 21
$oo' = 111 : 11\bar{1}$	15	68 31 — 69 4	68 42	68 42
$oo' = 111 : \bar{1}\bar{1}1$	3	110 59 —111 28	111 14	111 18
$or = 111 : 011$	2	36 2 — 36 26	36 14	36 6
$ao = 100 : 111$	7	53 39 — 54 2	53 51	53 54
$oo' = 111 : \bar{1}11$	9	71 58 — 72 19	72 12	72 12
$pr = 110 : 011$	3	59 36 — 60 7	59 49	59 54
$pq = 110 : 101$	4	58 41 — 59 18	59 50	58 59
$rq = 011 : 101$	4	60 54 — 61 23	61 9	61 7
$aq = 100 : 101$	8	43 37 — 43 59	43 48	43 46
$cq = 001 : 101$	11	45 58 — 46 31	46 15	46 14
$oo = 111 : 1\bar{1}\bar{1}$	7	107 34 —107 56	107 49	107 48
$cr = 001 : 011$	3	45 30 — 45 59	45 34	45 42
$br = 010 : 011$	2	44 12 — 44 34	44 23	44 18
$ap = 100 : 110$	4	44 7 — 41 46	44 31	44 28
$bp = 010 : 110$	3	45 16 — 45 49	45 29	45 32

In physical and optical properties, the crystals closely resemble those of dextrorotatory camphorsulphonic chloride, with which they are isomorphous; their fracture is conchoidal, and a few chance fragments chipped off the crystals showed a biaxial interference figure, the axial angle of which was found to be 35° on measurement with a micrometer in the eye-piece of the microscope. This value is practically identical with that given by the butterfly twin crystals of the inactive isomeride. The double refraction is positive and fairly strong.

A comparison of the axial ratios of the crystals of this substance with those of detrorotatory camphorsulphonic chloride show that the two compounds, as was to be expected, are isomorphous.

$C_{10}H_{15}O{\cdot}SO_2Cl$ .... $a : b : c = 0{\cdot}9980 : 1 : 1{\cdot}0368$
$C_{10}H_{15}O{\cdot}SO_2Br$ .... $a : b : c = 0{\cdot}9816 : 1 : 1{\cdot}0249$

Both substances crystallise in group six of Groth's classification, exhibit the same forms, and have almost identical axial ratios. The similarity in geometrical properties is also extended to the physical characters; both have fairly strong positive double refraction, and their optic axial angles are of the same order of magnitude. The similarity is, as has been shown above, extended even to the behaviour of mixtures of the lævo- and dextro-isomerides.

The hemihedral character of the crystals is clearly shown by the frequent occurrence of whole crops of tetrahedra; this must be regarded as conclusive evidence of their sphenoidally hemihedral character. On these tetrahedral crystals, the four faces of one semi-form of the octahedron {111} is largely developed, whilst the faces of the other semi-form are very small; this particular selection of four faces is not a fortuitous one, inasmuch as crystals do not occur which exhibit largely developed a selection of four faces of the octahedron {111} other than that demanded by this particular hemihedrism. The isomorphism of dextrorotatory camphorsulphonic chloride and bromide is thus still complete, although the latter sometimes occurs in octahedra whereas the former does not.

Bromocamphorsulphonic Bromide, $C_{10}H_{14}BrO{\cdot}SO_2Br$.

On triturating the air-dried, crystalline ammonium bromocamphorsulphonate, prepared in the manner previously described (p. 356), with a slight excess of the theoretical quantity of phosphorus pentabromide, and then keeping the mixture for about half an hour to ensure the completion of the action, a pale brown pasty mass is obtained; on slowly stirring this into powdered ice, the crude sulphonic bromide separates as a granular powder, which is collected on a filter and dissolved in chloroform; the solution is then washed, dried, and the chloroform distilled off. As the oily residue soon solidifies to a hard mass of crystals which is not easily washed, it is best to add some dry ether while it is still hot; the sulphonic bromide is then deposited as an almost colourless, crystalline powder, which is separated by filtration; the yield is at least 60 per cent. of the ammonium salt taken, and further quantities can be obtained from the ethereal mother liquors.

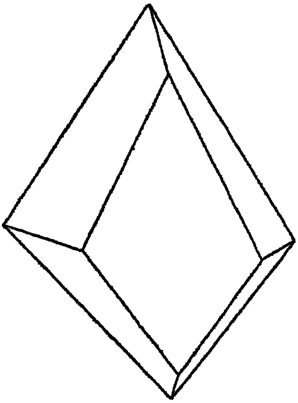
An analysis was made with a portion which had been recrystallised and then dried at 100°.

0·1784 gave 0·2068 CO_2 and 0·0606 H_2O. C = 31 6; H = 3 8.
$C_{10}H_{14}BrO{\cdot}SO_2Br$ requires C = 32·1; H = 3·7 per cent.

Bromocamphorsulphonic bromide has no definite melting point; when slowly heated, it begins to decompose at about 137°, but does not melt completely until near 145°; if, however, the tube containing the substance be plunged into sulphuric acid at 140°, complete liquefaction does not occur until the temperature rises to about 147°. It is very readily soluble in chloroform, benzene, and ethylic acetate, but comparatively sparingly in boiling light petroleum, from which it separates in fern-like crystals; it is only slowly hydrolysed by boiling with water.

From cold chloroform or ethylic acetate solutions, bromocamphorsulphonic bromide is deposited in massive transparent pyramids (Fig. 4) or flat plates with the edges replaced; these crystals have a vitreous lustre, and their faces, which are not very brilliant even when first taken from the mother liquor, slowly become duller on exposure to dry air. On decanting the solution and washing the crystals with ether, a very remarkable phenomenon occurs; as the layer of ether adhering to the solid evaporates, the crystals fly to pieces, emitting a very distinct crackling sound, the fragments in some cases being projected to a distance of several feet. The small pieces into which any particular transparent crystal are thus divided are quite dull and opaque.

FIG. 4.



This disintegration seems to be caused by the reduction in temperature attending the evaporation of the ether, for, if the vessel containing the crystals be inverted on a piece of filter-paper immediately after pouring off the ether, so as to check the rapid evaporation, the crystals can be preserved in a transparent state. Apparently the phenomenon is not due to polymorphism, because it occurs either on cooling or heating the crystals; if a beaker containing a quantity of crystals, covered by a layer of mother liquor several centimetres in thickness, be put on a water bath, the disruption of the crystals is so violent that some of the liquid is projected from the beaker. The curious behaviour of the crystals on change of temperature is most probably due to their being very brittle and possessing a large coefficient of thermal expansion.

Attempts were made to determine the geometrical constants of the crystals, but with little result, the reasons being principally the following:—When a well-developed crystal had been preserved intact until mounted on the Fuess goniometer, it very often disintegrated before its measurement was possible, owing to heating by the lamp. Further, it was found that no two faces on the crystals were parallel, and that consequently their measurement, even under favourable conditions, would have been attended with difficulty; it was also almost impossible to obtain completely developed crystals. Although measurements were made on about 20 crystals, the data were insufficient to permit of the orientation of the various faces; the absence of pairs of parallel faces points to the crystalline system being the extremely rare hemihedral subdivision of the anorthic system, and further measurements are, therefore, being undertaken in order to try and ascertain if this be so.

The crystals are very brittle, and have one good cleavage; through a cleavage plate, one axis of a biaxial interference figure emerges at the edge of the field commanded by a $\frac{1}{4}$-in. objective, and in an unsymmetrical position to the faces bounding the plate. On cooling a little of the warm, syrupy ethylic acetate solution of the substance under a cover slip on a microscope slide, crystalline skeletons separate, and the acute bisectrix of these is perpendicular to the cover slip. The optic axial angle in air for sodium light was found to be about 66° on measurement with a micrometer eye-piece; the double refraction is positive and fairly strong, and the dispersion is considerable.

The specific rotation of bromocamphorsulphonic bromide is $[\alpha]_D = +143°$; a chloroform solution of 2 9219 grams of the substance made up to 25 c.c, and examined at 12° in a 2-decimetre tube, gave $\alpha_D = +33° 26'$ as the average of six concordant observations.

Chlorocamphorsulphonic Bromide, $C_{10}H_{14}ClO{\cdot}SO_2Br$.

This substance is prepared from ammonium chlorocamphorsulphonate which, in its turn, is produced from chlorocamphor by the method fully described in the case of the corresponding salt of the bromosulphonic acid; the treatment of the ammonium salt with phosphorus pentabromide, and the isolation of the sulphonic bromide by extracting with chloroform, do not require detailed description. The residue obtained on evaporating the chloroform solution is a brown oil, which, when cooled in a freezing mixture, partially solidifies to a mass of crystals; these are collected by the aid of the pump, and the residue is repeatedly recrystallised from a mixture of chloroform and ether, animal charcoal being added to remove the brown impurities which adhere very tenaciously.

The pure substance crystallises from chloroform in massive, fern-like crystals, from a mixture of benzene and petroleum in transparent plates, and from boiling light petroleum in long, slender needles; like the bromosulphonic bromide, it has no definite melting point, but begins to sinter at about 134°, and melts completely at about 145°, rapid effervescence taking place; if heated very quickly from about 140°, it decomposes and melts fairly sharply at 145—147°. It is only slowly hydrolysed by boiling with water, and its solubility in the various organic solvents is much the same as that of the corresponding bromosulphonic bromide.

The specific rotation of the chlorosulphonic bromide is $[\alpha]_D = +129{\cdot}8°$; 2·1022 grams of substance were dissolved in chloroform, the solution made up to 25 c.c., and examined at 11° in a 2-decimetre tube; $\alpha_D = +21° 50'$ as the average of 10 concordant observations.

When chlorocamphorsulphonic bromide is dissolved in benzene, and the solution allowed to evaporate spontaneously, the substance is deposited in lenticular plates, of which the edges are at right angles; the corners are rounded owing to the curvature of the two faces of the plates. These faces are perpendicular to an acute bisectrix, and the optic axes are visible under an oil immersion objective; the interference figure is the normal orthorhombic one, and the optic axial angle in air for sodium light is about 74°; the double refraction is positive and strong, but the dispersion is small. No goniometrical measurements could be made owing to the curvature of the faces.

It is interesting to note the great crystallographical dissimilarity between the sulphonic chlorides of chlorocamphor and bromocamphor on the one hand, and the corresponding sulphonic bromides on the other. The former crystallise with readiness in large, well-defined isomorphous octahedra, which allow of easy and accurate measurement, whilst the latter crystallise with less readiness yielding ill-defined crystals, the crystallographic dimensions of which will only be determined with great difficulty. We cannot assert, however, that all four substances are not isomorphous; the optical characters of chlorocamphorsulphonic bromide point, in fact, to its belonging to the same system as the two sulphonic chlorides; it is very difficult, however, to reconcile the very exceptional behaviour and crystallographic properties of bromocamphorsulphonic bromide with those of the other three substances of the same type which we have examined.

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XLIII.—π-Halogen Derivatives of Camphor.

By F. STANLEY KIPPING, Ph.D., D.Sc., and W. J. POPE.

THE sulphonic chlorides and bromides of camphor, α-chlorocamphor, and α-bromocamphor, which we have described in former papers (Trans., 1893, 63, 548, and this vol.. p. 354), when heated alone at temperatures below 180°, are decomposed into sulphur dioxide and simple halogen derivatives of camphor; this change may be represented by the equation

$$C_{10}H_{14}XO{\cdot}SO_2Y = C_{10}H_{14}XYO + SO_2,$$

in which X represents H, Cl, or Br, and Y is Cl or Br.

The compounds prepared in this way are seven or eight in number, namely, two monochlorocamphors (dextrorotatory and racemic or inactive), two monobromocamphors (dextrorotatory and racemic), one dichlorocamphor (dextrorotatory), one dibromocamphor (dextrorotatory), and one, probably two, dextrorotatory chlorobromocamphors.

As these substances are not identical with the corresponding halogen derivatives of camphor which are already known, we propose to distinguish them, at any rate provisionally, by using the letter π (recalling their pyrogenic formation) to denote that halogen atom (Y) which, originally, is contained in the sulphonic group; in the case of the new di-halogen derivatives, therefore, the one halogen atom is distinguished by π, the other (X) by α, the sulphonic derivatives themselves having been prepared from the ordinary halogen compounds which are usually classed as α-derivatives.

For the sake of clearness, we give, in the first place, a list of those chloro-, bromo-, and chlorobromo-derivatives of camphor, containing one or two atoms of halogen, which have been prepared up to the present time.

The table (p. 372) includes, we believe, all the simple chloro- and bromo-derivatives of camphor, containing one or two atoms of these halogens, which have been described; it is possible—even probable—however, that of all the above mono-halogen compounds, only the α-, i-, and π-derivatives have any real existence, and we hope in the near future to curtail this formidable list by proving this to be the case.

The preparation of the π-halogen derivatives described in this paper is, as a rule, an extremely simple operation, as it is only necessary to heat the sulphonic chloride or bromide for a short time at a temperature ranging from 140° to 180° until the evolution of sulphur dioxide is practically at an end; in some cases, a portion

	Prepared by	M. p.	Rotatory power.
Monochlorocamphor, $C_{10}H_{15}ClO$	Wheeler, *Annalen*, 146, 81 Cazeneuve, *Compt. rend.*, 109, 229	95° 124—125°	— $[\alpha]_D$ = +40°
α- " "	Cazeneuve, *Bull. Soc. Chim.*, 38, 9	96°	$[\alpha]_j$ = +90°†
β- " "	" " " 39, 116	100°	$[\alpha]_D$ = +90°
π- " "	Kipping and Pope, this paper	189—189·3°*	$[\alpha]_D$ = +99·9°
π- " " (inactive)	" " "	188—188·3°	Inactive.
Monobromocamphor, $C_{10}H_{15}BrO$	Cazeneuve, *Compt. rend.*, 109, 444	144—145°	$[\alpha]_D$ = +40°
α- " "	Maisch, *Jahresb.*, 1873, 499	76°	$[\alpha]_D$ = +132—139°
β- " "	Marsh, *Trans.*, 57, 82	61°	$[\alpha]_D$ = +29·4°
i- " " (inactive)	Haller, *Compt. rend.*, 105, 66	51°	Inactive.
π- " "	Kipping and Pope, this paper	98·4°	$[\alpha]_D$ = +116°
π- " " (racemic)	" " "	92·7°	Inactive.
α-Dichlorocamphor, $C_{10}H_{14}Cl_2O$	Cazeneuve, *Bull. Soc. Chim.*, 37, 451	96°	$[\alpha]_j$ = +57·3°
β- " "	" " " 38, 8	77°	$[\alpha]_j$ = +60·6°
απ- " "	Kipping and Pope, this paper	118—118·5°	$[\alpha]_D$ = +86·7°
α-Chlorobromocamphor, $C_{10}H_{14}ClBrO$	Cazeneuve, *Bull. Soc. Chim.*, 44, 116	98°	$[\alpha]_j$ = +78°
β- " "	" " " 44, 118	51·5°	$[\alpha]_j$ = +51°
απ- " "	Kipping and Pope, this paper	188—188·5°	$[\alpha]_D$ = +85·2°
πα- " "	" " "	182—183° ?	$[\alpha]_D$ = +107·5° ?
α-Dibromocamphor, $C_{10}H_{14}Br_2O$	Kachler and Spitzer, *Monatsh.*, 3, 205	61°	—
β- " "	" " " 4, 486	115°	—
απ- " "	Kipping and Pope, this paper	152—153°	$[\alpha]_D$ = +98·8°

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* The melting points given by us are not corrected.

† We take this opportunity of correcting the erroneous assertion that the two monochlorocamphors described by Cazeneuve are polymorphous modifications of one substance. Lehmann (*Molekularphysik*, 1, 664) cites the conversion of β- into α-chlorocamphor on heating with alcoholic potash as an instance of irreversible change; Arzruni (*Physik. Chemie d. Krystalle*, 1893, 57), in noting this statement, interprets it as meaning that α- and β-chlorocamphor are monotropic modifications—an obviously erroneous reading.

of the product sublimes during the process, and is deposited in crystals on the cooler parts of the vessel, the rest being easily obtained in a pure condition by recrystallisation or by distillation in steam. In a few instances, however, notably in the preparation of dextrorotatory π-chlorocamphor and in the decomposition of bromocamphorsulphonic chloride, a large quantity of carbonaceous matter is formed as the result of secondary actions, and the product is not easily isolated. In the case of optically inactive π-monochlorocamphor, the action takes an unusual course, inasmuch as a large proportion of the product consists of a pleasant-smelling oil from which the crystalline π-chloro-compound may be separated by fractional distillation. Finally, it is interesting to note that the sulphonic bromides undergo decomposition at a lower temperature than the corresponding sulphonic chlorides, and give virtually a theoretical yield of the π-halogen derivatives, whereas, in the decomposition of the sulphonic chlorides, the yield is comparatively small owing, apparently, to the occurrence of secondary changes.

As regards physical properties the π-halogen derivatives are, on the whole, very similar to the corresponding compounds already known. The π-monohalogen derivatives dissolve freely in all ordinary organic solvents, from which, with the exception of inactive π-monochlorocamphor, they are deposited in small needles or prisms; the π-dihalogen derivatives, on the other hand, are less readily soluble, and are easily obtained in large well-defined orthorhombic prisms. All the π-halogen derivatives sublime readily, usually at temperatures below their melting points, and they are all volatile in steam.

In spite of the fact that the number of mono- and di-halogen derivatives of camphor now known amounts to at least 16, and the great probability that all these compounds are related to one another in an extremely simple manner, there does not seem to be any regularity in the melting points of the halogen derivatives themselves, or any connection between the melting points of the π-derivatives and those of the sulphonic compounds from which they are produced. Dextrorotatory π-monochlorocamphor, for example, melts at 139—139·3°, and the corresponding bromo-compound at 93·4°, a difference of 46°; in the case of the ordinary α-monohalogen derivatives, however, the difference in melting point is only 20°; again, απ-dichloro- and απ-dibromo-camphor melt at 117·5—118·5° and 152·5—153° respectively, whereas in the case of the corresponding α-dihalogen compounds the dibromo-derivative melts at a lower temperature than the dichloro-derivative. A similar want of regularity is observed on comparing the melting points of the π-derivatives with those of the sulphonic compounds from which they are derived; but here, unfortunately, some of the data are rendered untrustworthy by the fact that the sulphonic bromides decompose at, or below, their melting points.

A very remarkable phenomenon is observed in the case of racemic and dextrorotatory π-monobromocamphor; these two compounds melt at practically the same temperature, namely, at 92·7° and 93·4° respectively, and the melting point of the one is not appreciably affected by the presence of the other; consequently all mixtures of the two substances have practically the same melting point, namely, 92·7—93·4°. A similar behaviour is met with in the case of inactive and dextrorotatory π-monochlorocamphor; the difference in melting point is only about 1°, and all mixtures of the two substances melt at 138—139°.

As is well known, the determination of a melting point in the ordinary manner is not a very accurate process, and even with one and the same apparatus and one and the same substance, the observed melting point varies slightly according to the way in which the operation is conducted; hence, in the case of compounds which melt at so nearly the same temperature as the two π-monochlorocamphors and the two corresponding bromo-compounds, it is almost impossible to observe any difference in melting points unless the two substances are directly compared. The results of experiments made in this manner at first indicated that the isomerides in question had exactly the same melting point (Proc., 1895, 39), as they liquefied simultaneously when the capillary tubes were heated together in one bath; these observations, however, proved to be not quite correct, probably owing to the fact that the active isomerides were not absolutely pure and liquefied slightly below their true melting points. When carefully purified samples of the two π-monochlorocamphors and of the two π-monobromocamphors, the melting points of which were constant, were examined, it was found that the optically inactive compound invariably melted before its active isomeride; the difference, however, was very small and did not exceed 1° in either case.

All these observations with the π-monohalogen compounds were made with a standard thermometer graduated to 0·2°, and in every case the temperature was raised extremely slowly. The active π-monobromo-compound melted absolutely sharply, and the active π-monochloro-derivative liquefied completely within a range of about 0·3°; the inactive compounds, however, especially the chloro-derivative, did not melt quite sharply even after about 20 recrystallisations, and the two mixtures which were examined showed a similar behaviour; it seems hardly possible that this slight sintering in the case of the inactive substances, could have been due to the presence of traces of the active compounds, since the addition of large quantities of the latter produced no appreciable effect; we are, therefore, inclined to adopt the view that the somewhat indefinite melting points of these inactive compounds is due to a change in crystalline form or is a specific property of the substances.

Unfortunately, owing to our inability to obtain the inactive π-chlorocamphor in a form suitable for crystallographic examination, we are unable to state positively that it is a true racemic compound; we consider it to be so, however, for the following reasons:—Optically inactive π-monobromocamphor, as is shown by crystallographic examination. is a true racemic modification, that is to say, it is a definite crystalline compound, and not a mere mixture of the two optical antipodes; since, therefore, the relation between optically inactive π-monochlorocamphor and its optical isomeride is, on the whole, very similar to that between racemic π-monobromocamphor and its optical isomeride, and the two optically inactive substances are so nearly related in composition and constitution, it is probable, judging from analogy, that the optically inactive chloro-compound is also a racemic modification.

Leaving the π-monochloro-derivatives out of consideration, there still remains the case of the π-monobromo-compounds, which we believe to be the first on record in which two substances, differing in crystalline form, have no effect on each other when melted together; in this respect they show the behaviour of isomorphous substances, a fact which is all the more remarkable when it is borne in mind to how great an extent the melting point of a substance is usually lowered by admixture with a stereochemical isomeride; it would be of interest, therefore, to ascertain whether this behaviour is shown by other organic compounds which are related to one another in the same way as these two derivatives of camphor.

The possible importance of cases of polymorphism amongst substances possessing optical activity in solution, in connection with the question of circular polarisation, has been recently pointed out by Jungfleisch and Léger (*Compt. rend.*, 1895, **120**, 325), and, in the course of this investigation, opportunities have occurred for studying substances of this nature. Several of the π-monohalogen derivatives of camphor are polymorphous, and the crystalline forms of the different physical modifications have been examined to some extent; we have, however, by no means exhausted the investigation of these highly interesting substances, and the facts recorded in this paper are merely those which were brought out during the ordinary examination of the new compounds. In one instance, namely in that of dextrorotatory π-monobromocamphor, two of the forms in which it exists are directly obtainable by crystallisation under different conditions, the one melting at about 60°, the other at 93·4°; the change of the less into the more stable modification at ordinary temperatures may be accomplished without the aid of heat, in a very simple manner, and as the change is accompanied by a marked alteration in form, clearly visible to the naked eye, the operation is a very suitable one for lecture demonstration.

In the majority of cases, only one of the modifications appears to be sufficiently stable at ordinary temperatures to allow of its preparation by crystallisation under the usual conditions; it is possible, however, that the experiments which are now in progress may show that other modifications may be obtained and kept, as in the case of dextrorotatory π-monobromocamphor.

As is well known, when a substance exists in polymorphous forms, the modification stable at the highest temperature is usually that possessing greatest geometrical symmetry; in this respect the π-monohalogen derivatives form no exception to the general rule, the modifications in question belonging to the cubic system, which has nine planes of symmetry, whilst those stable at ordinary temperatures are either tetragonal or orthorhombic with five and three planes of symmetry respectively.

The $\alpha\pi$-dihalogen derivatives which we describe are evidently substances of analogous constitution, judging both from their methods of formation and from their crystallographic properties; they form a very well-defined, isomorphous series, the angular dimensions and the axial ratios of the various members being very nearly the same.

The specific rotations of all the new optically active π-halogen compounds have been determined, and the values are considerably higher than those for the previously known isomerides; the experimental data thus obtained, and those collected during the study of the sulphonic chlorides and bromides, together with the recorded values for the known halogen derivatives, are sufficiently numerous to afford material for a careful consideration of the relation between chemical composition and specific rotatory power; this matter has already received our attention, but, in view of its importance, we reserve its discussion for a future paper.

The main object of our work in this particular field, namely to throw some light on the still problematic constitution of camphor, is advanced but little by the facts recorded below; hitherto we have been led to neglect the purely chemical side of the question by the constant occurrence, in the substances prepared, of interesting physical properties, well worthy of a much more exhaustive study than we have yet been able to bestow.

Attention may, however, be drawn to the more important chemical facts which have been established, one being that on sulphonating camphor, the sulphonic group does not displace the particular hydrogen atom which is eliminated on converting camphor into the ordinary α-monohalogen derivatives; this follows, of course, from the non-identity of the π- and the α-halogen compounds, and also from the fact that on reducing bromocamphorsulphonic acid with zinc dust and ammonia, it is converted into a sulphonic acid, the sulphonic chloride of which yields a π-monochlorocamphor, identical with that obtained from the camphorsulphonic acid prepared by direct sulphonation of camphor. It has also been found that the π-halogen atom, which is introduced with the aid of the sulphonic group, is eliminated, on reduction, much less readily than the α-halogen atom, inasmuch as απ-dichlorocamphor is converted into π-monochlorocamphor on treatment with nascent hydrogen.

The further investigation of these new halogen derivatives, and of the sulphonic compounds from which they are derived, is in progress, and the results which have already been obtained (Proc., 1895, 33), give promise of others even more interesting as the work advances.

Dextrorotatory π-Monochlorocamphor, $C_{10}H_{15}ClO$.

Pure dextrorotatory camphorsulphonic chloride (m. p. 137·5°), prepared by the method already described (this vol., p. 358), is heated in quantities of about 2 grams at a time, in a loosely corked test-tube dipping into a metal bath, the temperature of which is indicated by a thermometer placed in the test-tube; decomposition commences at about 160—170°, and a brisk effervescence sets in at about 175°, but at the same time the liquid darkens considerably, and traces of hydrogen chloride seem to be evolved; after heating for about 10 minutes, the temperature having been slowly raised to about 190°, the evolution of gas practically ceases. The product, a thick, tarry mass, is then subjected to distillation in steam, whereupon an almost colourless, pleasant-smelling oil passes over, a large quantity of pitchy matter remaining in the distilling flask. The oil soon becomes pasty, and after a few days solidifies to a crystalline mass, which is separated and spread on porous earthenware to free it from adhering oil; the crude dextrorotatory π-monochlorocamphor thus obtained is finally purified by crystallisation from dilute alcohol, or from light petroleum.

0·1432 gave 0·3400 CO_2 and 0·1053 H_2O. C = 64·75; H = 8·17.
Theory. C = 64·37; H = 8·04 per cent.

The yield of π-monochlorocamphor by the above method is comparatively small, amounting only to about 15 per cent. of the theoretical, the main product consisting of a pitch-like mass, which did not invite investigation.

Dextrorotatory π-monochlorocamphor melts at 139—139·3° and sublimes in needles, even at temperatures below its melting point; it is volatile in steam, and distils under ordinary atmospheric pressure when heated in small quantities at a time, only slight decomposition taking place. It is practically odourless at ordinary temperatures, but when heated it evolves vapours which have a faint, camphor-like smell, and at the same time a slight odour of turpentine. Although it is not so readily soluble as inactive π-monochlorocamphor (see below), it nevertheless dissolves very freely in all ordinary organic solvents, even in cold light petroleum, and for this reason could not be obtained from its solutions in well-defined crystals; it is usually deposited from dilute alcohol in long, flat needles, and from petroleum in small, acicular crystals, but from a mixture of petroleum and ethylic acetate it is sometimes obtained in long, transparent, flattened prisms, terminating in ragged ends. The best-defined crystals, however, were obtained from the porous earthenware which had been used in the purification of the crude product. On exposing the clean side of the ware to a very gentle heat for some weeks, the compound slowly sublimed on to the outside in well-defined prisms. These crystals were about 1 mm. in length and 0·1 mm. in diameter, and were simply hollow prismatic shells; the extinctions in the prism zone were straight, but no trace of an interference figure could be discerned through them. On measuring the angles in the prism zone, several were found to be 45°, thus indicating that the crystals were tetragonal.

On melting a little of the substance on a microscope slide under a cover slip, and allowing it to cool, the solidified mass, whilst still warm, is seen to be perfectly isotropic; as it cools still further, however, cracks are seen to gradually run across it, and the crystalline plates become feebly anisotropic. The double refraction increases to such an extent that, on rotating the nicols, the plate may be seen to consist of a number of individuals which do not all extinguish at the same time; the birefringence is, however, still very weak. Suddenly, as the temperature continues to fall, the crystalline form of the substance commences to change at one corner of the plate, and a new growth runs rapidly across; the new crystals thus obtained possess fairly strong double refraction, and apparently belong to the tetragonal system, as the interference figure of a uniaxial crystal can be seen through some of the individuals of which the plate is composed. The examination of the interference figure is complicated by the fact that the optic axis always appeared at the edge of the microscopic field, and could not be got central. The cross in the centre of the figure appears to open slightly as the nicols are rotated; this, however, is very slight, and may be attributed to the same cause as that which makes many tetragonal substances appear biaxial, with a small axial angle. On reheating the cooled preparation, the same series of changes occurs, but in the reverse order; this substance therefore affords a case of enantiotropy.

The above observations show that dextrorotatory π-monochlorocamphor is dimorphous, crystallising in the cubic system at high, and in another system, apparently the tetragonal, at ordinary, temperatures; the polymorphism is, however, not so well marked as in the case of the active π-monobromocamphor described below, inasmuch as the change of one modification into the other proceeds less regularly, and does not give such large and easily distinguished crystalline individuals.

The specific rotation of dextrorotatory π-monochlorocamphor is $[\alpha]_D = +99{\cdot}88°$; a solution of 0·5882 gram in chloroform, made up to 25 c.c., and examined in a 2 decimetre tube, having given a rotation of $\alpha_D = +4° 42'$ as the mean of eight concordant observations.

Inactive π-Monochlorocamphor.

Since the two optically active modifications of camphorsulphonic chloride do not form a very definite racemic compound, and since, moreover, the sulphonic chloride obtained from the product of the sulphonation of camphor contains a larger proportion of the dextro- than of the lævo-rotatory isomeride, it was necessary to carefully recrystallise a large quantity of the sulphonic chloride, in order to separate as far as possible the excess of the dextrorotatory substance from the samples to be employed in the preparation of inactive π-monochlorocamphor; otherwise, should the inactive π-chlorocamphor be as readily soluble as the active isomeride just described, its separation from the latter would not be easily accomplished. For this reason, a considerable quantity of the crude sulphonic chloride was repeatedly recrystallised from cold ethylic acetate, and any tetrahedra which were deposited were separated mechanically. Having thus obtained a preparation which had doubtless a comparatively small rotatory power, the substance was heated in loosely corked test-tubes in quantities of about 2 grams at a time; its behaviour was very similar to that of the active sulphonic chloride, except that effervescence seemed to set in at a rather lower temperature, and only a trace of, if any, hydrogen chloride was evolved; after heating for about 15 minutes, slowly raising the temperature to about 190°, effervescence ceased, and the thick, dark, oily residue was subjected to steam distillation.

The pale yellow oil which collected in the receiver had a very pleasant, sweet odour, quite unlike that of camphor; as it did not solidify, it was extracted with ether and fractionally distilled under a pressure of 100 mm. It began to boil at about 160°, and the thermometer then rose continuously to about 185°, by which time the whole had passed over: the two fractions in which the distillate had been collected, at once deposited a considerable quantity of a crystalline substance which looked like camphor, and which was separated by filtration; further quantities of this solid were isolated by fractionating the oily mother liquors under atmospheric pressure, and then cooling the several fractions (220—240°, 240—255°, 255—270°) in a freezing mixture, when that of highest boiling point solidified almost completely.

The crystalline product was now freed from oil with the aid of porous earthenware, recrystallised from dilute alcohol, and dried over sulphuric acid. Analysis showed it to be a monochlorocamphor.

0·1619 gave 0·3794 CO_2 and 0·1205 H_2O. C = 63·91; H = 8·27.
0·1438 „ 0·3383 „ „ 0·1096 „ C = 64·16; H = 8·47.
0·2754 „ 0·2155 AgCl. Cl = 19·35.
Theory: C = 64·37; H = 8·04; Cl = 19·00 per cent.

A sample was then examined in the polarimeter, in order to ascertain what excess, if any, of the dextrorotatory chlorocamphor was present, as it was probable that the sulphonic chloride which had been used in its preparation was feebly dextrorotatory; a solution of 0·9602 gram in chloroform, diluted to 25 c.c., and examined in a 2 decimetre tube, gave $\alpha_D = +0° \ 23'$, from whence $[\alpha]_D = +4·99°$.

The excess of the dextrorotatory compound was therefore about 5 per cent. The sample was then fractionally recrystallised from dilute alcohol, the middle fraction collected, and again recrystallised; the middle fraction from this second operation was employed for an examination of the properties of the substance.

Although it is impossible to say with certainty that the substance prepared in this way is a definite racemic compound, owing to its somewhat ill-defined properties, we believe that this conclusion accords best with our observations. The optically inactive π-monochlorocamphor melts at 138—138·3°, but sinters slightly at about 136°, even after repeated recrystallisation; it is readily soluble in all ordinary organic solvents, and, like the dextro-modification, it sublimes readily, is volatile in steam, and distils without decomposition under atmospheric pressure; its vapours have a camphor-like odour, but the substance itself has only a very faint, sweet smell at ordinary temperatures. It usually crystallises from cold dilute alcohol in fern-like forms, similar in appearance to flowers of camphor, and quite different from the long, flattened prisms of the active modification;

if, however, these fern-like crystals are left in contact with the mother liquors, they are sometimes slowly converted into compact, opaque, crystalline masses (A), which on microscopic examination are seen to consist of slender needles having straight extinction. If, on the other hand, these fern-like crystals are left on porous earthenware for some weeks, part changes into highly lustrous, well-defined crystals, which are seen embedded in the remaining camphor-like mass. These lustrous crystals are compact pyramids, quite distinct in shape from the thin needles mentioned above. It may be noted, too, that in one case a sample of the compact opaque crystals (A), which were kept for some weeks in a dessicator, underwent a complete change in outward appearance, minute needles having grown from the central compact mass, from which they projected in all directions. The melting point of all these forms was the same, namely, 138—138·3°.

As in the case of the optically active modification, some of the best defined crystals of inactive π-monochlorocamphor were obtained from the porous earthenware on which the crude product had been spread; these consisted of slender prisms showing straight extinction, and, like the other forms, melted at 138—138·3°.

The behaviour of inactive π-monochlorocamphor, on heating, is remarkable; as stated above, all the samples obtained by crystallisation or by the spontaneous change of such samples melt not quite sharply at 138—138·3°, and, on quickly cooling the melting point tube, by taking it out of the sulphuric acid, the solidified substance fuses again at the same temperature; if, however, the tube be allowed to remain in the sulphuric acid while the latter cools slowly to the ordinary temperature, the substance sometimes does not solidify until the temperature falls to about 20°, and, on again heating, it melts at 25—28°. Inactive π-monochlorocamphor is therefore dimorphous, the two forms differing in melting point by about 110°. So large a difference in melting point between two such modifications is, we believe, unique, as the various polymorphs of one substance usually melt within a few degrees of each other, and only in very few cases does the difference in melting point exceed 20°.

This peculiar behaviour towards heat would seem to stamp optically inactive π-monochlorocamphor as physically distinct from its active isomeride, and, for this and other reasons already mentioned, the conclusion that the inactive substance is a true racemic compound would seem to be a legitimate one.

Owing to the incomplete separation of the solid inactive π-monochlorocamphor from the oil by which it was accompanied, a comparatively small yield is obtained, although the quantity of the crude oily mixture which distilled in steam amounted to rather more than

50 per cent of the weight of sulphonic chloride taken; the rest was converted into carbonaceous matter. The formation of an oil in such large quantities in this case is certainly an interesting fact, since no similar product was obtained in the decomposition of optically active camphorsulphonic chloride. An analysis of the oil has not yet been made, as, with the quantity at our disposal, it could not be completely separated from the chlorocamphor by distillation; it was found, however, to be readily oxidised by potassium permanganate in cold acetic acid solution, and also by nitric acid. When it was heated with dilute nitric acid in a reflux apparatus, a large quantity of chlorocamphor collected on the cooler parts of the condenser, and the oil gradually passed into solution; from this solution, a considerable quantity of a crystalline acid, which was sparingly soluble in boiling water, was isolated, and oxalic acid and an oily product were also obtained; these oxidation products will be further examined.

Dextrorotatory π-Monobromocamphor, $C_{10}H_{15}BrO$.

On heating dextrorotatory camphorsulphonic bromide (this vol., p. 364) in a beaker placed in a metal bath and covered with a clock-glass, decomposition sets in just as the crystals begin to melt, and, on raising the temperature to about 155°, a very vigorous evolution of sulphur dioxide commences; when treating quantities of about 4 grams at a time, the conversion into π-monobromocamphor is complete in about 5—7 minutes. No fumes of hydrogen bromide are observed during the operation, and the product is only slightly coloured; it is unnecessary, therefore, to distil in steam, as the compound is easily purified by recrystallisation.

An analysis of the pure preparation showed it to be a monobromocamphor.

0·1503 gave 0·2874 CO_2 and 0·0937 H_2O. C = 52·15; H = 6·93.
Theory: C = 51·95; H = 6·5 per cent.

The yield in this case is practically theoretical, no carbonaceous matter or secondary products being formed; this fact is all the more striking when it is borne in mind that, in the decomposition of the corresponding sulphonic chloride, the yield of dextro-π-monochlorocamphor is comparatively small.

For the determination of the rotatory power of the substance, a solution of 1·5301 grams in chloroform, diluted to 25 c.c., was examined at 15° in a 2 decimetre tube; the average of nine concordant observations gave $\alpha_D = +14° \ 12'$, whence the specific rotation $[\alpha]_D = +116·01°$.

Optically active π-monobromocamphor is volatile in steam and sublimes readily; it dissolves freely in all ordinary organic solvents, and is best recrystallised from light petroleum or dilute alcohol, from both of which it separates in the cold in long, colourless needles; the melting point of the crystals obtained in this way is usually 93·4°, but the compound is di- or poly-morphous, and shows the following interesting behaviour.

On allowing its solution in warm dilute alcohol to crystallise rapidly, but without agitation, moss-like needles are sometimes deposited; if these crystals be taken out of the solution and spread on porous earthenware, they melt at about 60—63°, but frequently change spontaneously into the modification melting at 93·4°, without any change in form visible to the naked eye; as a rule, however, without any very obvious alteration in the conditions of the experiment, the crystals directly deposited from the alcoholic solution melt at 93·4°. In one experiment, in which a warm solution had been put to crystallise slowly during the night, these two modifications were deposited side by side, the smaller needles from the upper layers melting at 93·4°, whereas a few larger ones, which were deposited at the bottom of the beaker, melted at about 63°. Although this extraordinary behaviour was only noted on one occasion, there is no doubt as to its correctness; it might, of course, be explained by assuming that all the crystals really consisted of the modification melting at 60—63°, but that the larger ones did not change into the form melting at 93·4° so readily as the smaller ones, and consequently remained unaltered during the operations attending their removal from the solution and introduction into the melting-point tube. This assumption, however, in our opinion, is not warranted, because the two kinds of crystals differed so much in appearance that they were thought to be different substances, and for this reason only were they melted separately; it must be concluded, therefore, that, at first, crystallisation took place at a temperature at which the modification melting at 60—63° is stable, but that, as the solution cooled, the conditions became favourable to the deposition of the form melting at 93·4°, the two crystalline varieties thus separating at different temperatures. This view is, we think, much more probable than that crystallisation occurred at the temperature of equilibrium between the two modifications, and is supported by the fact that the two kinds of crystals were not, to our knowledge, touching each other, but, from the loosely aggregated character of the crystalline mass (which resembled that assumed by metadinitrobenzene crystallising from its dilute solution in weak alcohol), might well have been quite apart, in which case, of course, the modification stable at the lower temperature would have been unable to induce the change of the less stable form.

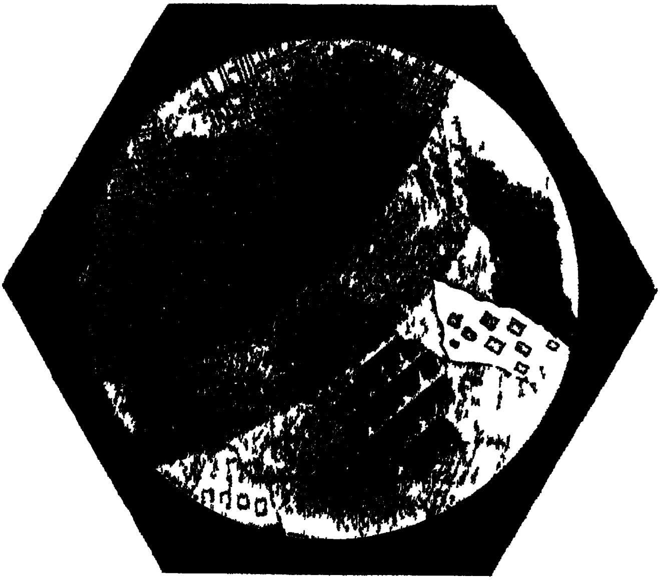
When dextrorotatory π-monobromocamphor is melted and then rapidly cooled from about 95°, by taking the tube out of the hot bath, the substance immediately solidifies, giving the modification melting at 93·4°; if, however, the tube containing the liquefied substance be allowed to remain in the bath until the temperature falls to about 50°, and is then taken out, the liquid solidifies on further cooling, giving the modification melting at about 60°; the melting point, however, is not very sharp, owing, doubtless, to partial change into the other form taking place.

The existence of two crystalline forms, and the change of one into the other, may be very easily demonstrated in the following manner. The substance is dissolved in such a quantity of warm dilute alcohol that crystallisation takes place readily on cooling a little; the test-tube containing the warm, clear solution is then rapidly cooled under the tap, stirring vigorously all the time; in this way, the modification of lower melting point is deposited as a granular powder, consisting of fern-like crystals; if, now, a fragment of the modification melting at 93·4° be dropped into the solution and the mixture stirred, the granular powder immediately changes into a bulky, moss-like mass of needles, totally different in appearance from the granular powder. This change sometimes occurs spontaneously, when the test-tube containing the liquid and crystals is allowed to stand at ordinary temperatures for a few hours.

On pouring some of the contents of the test-tube on to a microscope slide before the change of the granular powder has been brought about, and then watching the crystals under a low power, the transformation is exceedingly interesting; on placing a crystal of the modification melting at 93·4° in contact with the edge of the liquid, the fern-like crystals rapidly change into small prisms; long needles then at once begin to form and gradually grow longer and longer, and, as they approach the prisms, the latter disappear, their place being taken a second or two later by a mass of the long needles. This would seem to indicate that the substance is trimorphous, and further evidence in favour of this view is adduced below. The curious disappearance of the prismatic crystals as the needles approach them is probably due to their solubility being greater than that of the needles; a similar phenomenon has been observed by Lehmann in the case of two of the modifications of ammonium nitrate.

On fusing a few milligrams of active π-monobromocamphor on a microscope slide under a cover slip, and then allowing it to cool, solidification to a cubic modification occurs while the slide is still hot; this modification crystallises in long needles with projecting branches on either side, and is completely isotropic. It may be conveniently observed orthoscopically under a ½-inch objective with the nicols crossed so as not quite to extinguish the light. After the preparation has cooled to nearly the ordinary temperature, a change in crystalline form is observed to start at one corner of the field and pass slowly across; the new modification is seen to consist of large numbers of small patches possessing fairly strong double refraction, so that the field is illuminated by interference colours of high orders. The crystals are uniaxial, the principal axis of many of the patches being perpendicular to the surface of the slide, and the double refraction is positive. The line of progress of this modification across the plate is followed very rapidly by another, the crystalline form apparently changing a second time; the new crystals thus obtained have the same outline as the patches of the first uniaxial modification, and the principal axis of the latter remains the principal axis of the new form which also has positive double refraction. The only apparent difference between these two uniaxial forms is that the magnitude of their double refraction is slightly different; the two forms may, therefore, ultimately be found to be structurally identical but possessing refractive indices which change considerably with the temperature. A rough representation of these various modifications undergoing change is given in the appended sketch (Fig. 1).

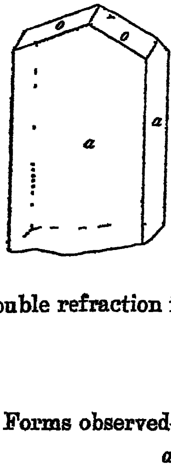
FIG. 1.



These changes may be conveniently observed macroscopically as they occur on the slide: the cubic modification is first seen to form and to sweep slowly across the slide converting the liquid into a transparent film; after a few seconds, part of the outside of the film becomes white and much less transparent, and this change also slowly extends across the plate; a millimetre or so behind this the second change in crystalline form occurs, and is seen to pass over the plate, rendering it even more white and opaque.

The uniaxial modification of active π-monobromocamphor which finally results from this series of changes is identical in form with that deposited from cold petroleum solutions. The latter consists of long, flattened, transparent prisms possessing a vitreous lustre; the faces are bright when the crystals are first removed from the solution, but on exposure to the air for a few hours, lose greatly in brilliancy. There is a great deal of internal striation parallel to the c-axis; as a rule, the crystals only exhibit faces in the prism zone, the ends being ragged, but sometimes they show several faces of the form $o\{111\}$ at one end; the faces are not very plane, and give bad images. On cutting a fragment perpendicular to the c-axis, a piece is obtained through which the interference figure of a uniaxial crystal can be seen; the double refraction is positive in sign and fairly strong.

FIG. 2.



Crystalline System: Tetragonal.

$a : c = 1 : 0{\cdot}4377.$

Forms observed—

a .... $\{100\}$ .... $\infty P\infty$,
o .... $\{111\}$ .... P.

The following angular measurements were obtained.

Angle.	No. of observations.	Limits.	Mean.	Calc.
$ao = 100 : 111$	14	67° 31′—68° 47′	68° 9′	—
$oo = 111 : 1\bar{1}1$	6	43 0—44 11	43 31	43° 42′

These being tetragonal crystals of a simple kind, two sets of indices are possible, the alternative set being $a\{110\}$ and $o\{101\}$; using these indices, the axial ratio is $a : c = 1 : 0\ 6190$. No trace of hemihedrism could be detected in the crystals, the faces of the form $o\{111\}$ never being reduced in number so as to accord with a tetragonal hemihedrism, although usually only two or three of them are present on the crystals.

On rapidly heating these transparent crystals by plunging the melting-point tube containing them into sulphuric acid at or above 60°, they immediately become opaque and then transparent again, but without breaking up; they do not melt, however, until the temperature rises to 93·4°.

Racemic π-Monobromocamphor, $C_{10}H_{15}BrO$.

The camphorsulphonic bromide which was required for the preparation of optically inactive π-monobromocamphor was obtained by the method described in the preceding paper (this vol., p. 359), and, for reasons already mentioned, samples containing as small an excess as possible of the dextro-modification were employed; such samples were prepared by repeatedly recrystallising portions of 4 or 5 grams and separating any of the characteristic tetrahedra of the active modification which were deposited. The approximately inactive substance, in quantities of about 2 grams at a time, was then heated at 145—155° in a beaker placed in a metal bath and covered with a clock glass; its behaviour was very similar to that of the active sulphonic bromide, sulphur dioxide was evolved with great rapidity, and very little charring occurred; after heating for about five minutes, the residue, which solidified on cooling, was purified by recrystallisation from dilute alcohol with addition of animal charcoal, and then from a mixture of ether and petroleum.

Analysis gave results agreeing with those required for a bromocamphor.

0·1691 gave 0·3226 CO_2 and 0·1014 H_2O. C = 52·03; H = 6·66.
$C_{10}H_{15}BrO$ requires C = 51·95; H = 6·5 per cent.

The yield of crude but practically pure inactive π-monobromocamphor obtained in this way is very nearly theoretical, and no secondary actions of any importance occur.

An optical examination of a preparation which had been crystallised two or three times showed it to be practically free from dextrorotatory π-monobromocamphor, inasmuch as a chloroform solution of 2·7600 grams diluted to 25 c.c. gave in a 2 decimetre tube $\alpha_D = +16'$, corresponding with $[\alpha]_D = +1·20°$; the quantity of the dextrorotatory modification was therefore only about 1 per cent.

Inactive π-monobromocamphor resembles the other π-monohalogen compounds in ordinary properties; it sublimes readily, is volatile in steam, and distils without decomposition under atmospheric pressure if heated in small quantities at a time. Although it dissolves freely in all ordinary organic solvents, it is certainly less soluble in boiling light petroleum than the corresponding active modification, and apparently also in other solvents; it also crystallises more readily and in a greater diversity of habits than the active isomeride, the crystals, moreover, being more massive. It separates from a mixture of light petroleum and ether, for example, in well-defined transparent prisms (see below), and from ether alone in very massive pyramids which easily attain 1 cm. in thickness. As ordinarily obtained from solution, it melts at 92·7°, but, like the active isomeride, it is undoubtedly dimorphous; when the liquefied substance is allowed to cool, it soon solidifies to a transparent, crystalline mass, which gradually becomes opaque as the temperature falls to about 40°; on heating again, the reverse change is observed, but the transparent crystals do not melt until the temperature rises to 92·7°. The exact temperature at which the change from the opaque to the transparent crystals occurred could not be ascertained, as the change appeared to be gradual.

When the melted substance solidifies under a cover slip on a microscopic slide, a well-defined, cubic modification is produced; this changes, however, as the temperature falls, in just the same way as in the case of the corresponding active π-bromocamphor, and a strongly anisotropic modification is produced. After this conversion, the film is seen to consist of a large number of small patches of a biaxial substance of large axial angle, the interference figure closely resembling that of the crystals obtained from petroleum solution.

The latter are massive, transparent prisms, which, when first taken from the solution, are highly lustrous, although their ends always terminate in very dull curved surfaces; more than one zone, namely that containing the four prism faces was never present, so that the crystalline system is unknown. The prism angle was found to be 69° 30′, as the mean of about 20 measurements. There is a fairly good cleavage parallel to one of the prism faces, and through a thin cleavage plate a biaxial interference figure can be seen; the two optic axes cannot be got into the field commanded by a $\frac{1}{12}$th-inch oil immersion objective, so that this prism face is probably normal to the obtuse bisectrix; the extinction through the prism faces is straight.

Active π-monobromocamphor belongs to the tetragonal system, and is consequently uniaxial, whilst its inactive isomeride crystallises in a biaxial system, probably the orthorhombic; there can, therefore, be no doubt that the latter is a true racemic modification, and the same would seem, by analogy of behaviour, to hold for the inactive π-monochlorocamphor. A series of melting-point determinations of mixtures of racemic and dextrorotatory π-monobromocamphor showed that the presence of one substance does not depress the melting point of the other, and indeed does not seem to effect it at all, inasmuch as all the mixtures melted at 92·5—93·5°; after the fused mixtures had solidified they melted, on re-heating, at the same temperature as before. This behaviour is much the same as would be expected of two isomorphous substances having almost the same melting point, as the curve plotted between the melting points and compositions of mixtures of isomorphous compounds is a straight line joining the melting points of the two constituents.

Melting-point determinations of mixtures of dextrorotatory and inactive π-monochlorocamphor showed that in this case also all the mixtures have the same point of fusion, namely 138—139°.

The parallel between the two pairs of substances is, therefore, very complete, and confirms us in our belief that the inactive π-monochlorocamphor is a true racemic compound.

aπ-Dichlorocamphor, $C_{10}H_{14}Cl_2O$.

The decomposition of chlorocamphorsulphonic chloride, unlike that of the other sulphonic chlorides which have been examined, is a very simple process, unaccompanied by any secondary actions; in preparing this dichlorocamphor, therefore, it is only necessary to heat the sulphonic chloride for about 15 minutes at 160—180°, and then recrystallise the residue from ethylic acetate or alcohol, with addition of a little animal charcoal; the yield is almost theoretical.

Analysis of the pure compound gave the following results.

0·1480 gave 0·2945 CO_2 and 0·0888 H_2O. C = 54·27; H = 6·66.
0·1907 „ 0·2476 AgCl (by the lime method). Cl = 32·12.
0·2220 „ 0·2863 AgCl „ „ Cl = 31·90.
$C_{10}H_{14}Cl_2O$ requires C = 54·34; H = 6·34; Cl = 32·03 per cent.

aπ-Dichlorocamphor crystallises from hot dilute alcohol and acetic acid in very long, slender needles, melting at 118—118·5°; it is very readily soluble in cold benzene and cold chloroform, but only sparingly in light petroleum, its solubility in all ordinary solvents being much less than that of the π-monohalogen derivatives described above. It has no smell, but when heated it gives off vapours which are very irritating, and the odour of which is quite unlike that of camphor; it sublimes readily, is volatile in steam, and may be distilled under atmospheric pressure if only small quantities be taken, although it decomposes on continued heating.

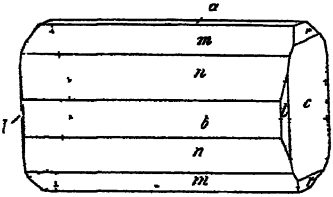
For the determination of the specific rotation, a chloroform solution containing 1·0376 grams was diluted to 25 c.c., and examined in a 2 decimeter tube at 12°; the rotation $a_D = +7° 12'$ whence $[a]_D = +86·74°$.

aπ-Dichlorocamphor is readily reduced when its alcoholic solution is treated with sodium amalgam, and if, after action has proceeded for some time, the solution be diluted and then cooled, colourless, slender needles will be deposited; this product, after recrystallisation from alcohol, melts at 139—139·3°, and is identical with the optically active π-monochlorocamphor obtained by the decomposition of dextrorotatory camphorsulphonic chloride.

On further treatment with sodium amalgam under the above-mentioned conditions, the optically active monochloro-compound seems to undergo no change, or, at any rate, reduction takes place very slowly. Of the two halogen atoms in απ-dichlorocamphor, therefore, the one which is originally introduced by chlorination is readily eliminated, whereas the π-chlorine atom, which comes from the SO_2Cl-group, and which is united with a different carbon atom, is more firmly held.

The crystals of απ-dichlorocamphor deposited by spontaneous evaporation of its cold ethylic acetate solution are somewhat elongated, flattened prisms, which attain a length of several centimetres (Fig. 3). They belong to the orthorhombic system, and show no indication of hemihedrism, although the substance is optically active in solution; this, however, is not surprising since no pyramid forms—the only ones affected by an enantiomorphous hemihedrism—are present. The forms in the prism zone are always much striated in the direction of the c-axis, the direction in which the crystals are elongated; the pinacoid b{010} is usually the dominant form, but the habit varies considerably with the conditions of growth. The prism forms n{130} and m{110} are the next largest developed, and give only medium reflections; the dome forms l{011} and r{101} are usually small, and give good results on measurement, whilst the pinacoid c is rather larger and not so good in character. The crystals have a dull, vitreous lustre, and, if grown quickly, are filled with internal striæ; those which develop slowly, however, are quite transparent and much more lustrous. The c-axis is parallel to the first mean line. The optic axial angle for sodium light was measured in glycerol through a section ground parallel to c{001}.

FIG. 3.



No. of observations.	Limits.	Mean angle in glycerol.	Calculated angle in air.
6	41° 29′—41° 32′	41° 30′	62° 18′

The dispersion is very small, and the double refraction is positive in sign and weak.

Crystalline System: Orthorhombic.

$a : b : c = 0{\cdot}6933 : 1 : 0{\cdot}3297$.

Forms present—

a	{100}	$\infty\breve{P}\infty$,
b	{010}	$\infty\bar{P}\infty$,
c	{001}	$0P$,
m	{110}	∞P,
n	{130}	$\infty\bar{P}3$,
l	{011}	$\bar{P}\infty$,
r	{101}	$\breve{P}\infty$.

The following angular measurements were obtained.

Angles.		No. of observations.	Limits.	Mean.	Calc.
nb	= 130 : 010	14	25° 37′— 25° 49′	25° 43′	25° 41′
nn	= $\bar{1}$30 : 130	16	51 10 — 51 34	51 26	51 21
mn	= 110 : 130	17	29 22 — 29 47	29 33	29 35
am	= 100 : 110	7	34 35 — 34 49	34 41	34 44
mm	= 110 : 1$\bar{1}$0	9	69 18 — 69 33	69 25	69 28
bm	= 010 : 110	21	55 3 — 55 39	55 16	—
bl	= 010 : 011	15	71 32 — 71 56	71 47	71 45
ll	= 011 . 0$\bar{1}$1	5	143 24 —143 41	143 32	143 30
ll	= 011 : 01$\bar{1}$	6	36 20 — 36 52	36 29	36 30
cl	= 001 : 011	4	18 1 — 18 25	18 11	18 15
ar	= 100 : 101	12	64 17 — 64 40	64 28	64 34
cr	= 001 : 101	24	25 11 — 25 47	25 26	—
rr	= 101 : $\bar{1}$01	8	50 31 — 51 2	50 47	50 52

aπ-Dibromocamphor, $C_{10}H_{14}Br_2O$.

Bromocamphorsulphonic bromide, like the other sulphonic bromides, decomposes very rapidly when heated at about 165°, and its conversion into *aπ*-dibromocamphor is readily accomplished in the usual manner; although only traces of hydrogen bromide are evolved, a small quantity of carbonaceous matter is produced during the operation, and the product is usually of a brown colour; as it does not volatilise in steam very rapidly, the *aπ*-derivative is most conveniently purified by a preliminary recrystallisation from hot acetic acid, a little nitric acid being added to destroy the coloured impurities; it is then obtained almost colourless, and may be further purified by crystallisation from dilute alcohol or acetone. The yield is practically theoretical.

Analysis gave the following results.

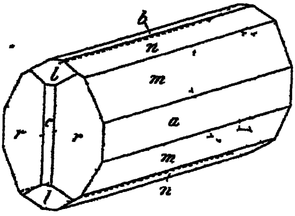
0·1804 gave 0·2538 CO_2 and 0·0801 H_2O. C = 38·4; H = 4·9.
0·2310 „ 0·2802 AgBr; Br = 51·57.
$C_{10}H_{14}Br_2O$ requires C = 38·7; H = 4·5; Br = 51·61 per cent.

απ-Dibromocamphor crystallises from hot dilute alcohol, acetone, or acetic acid in long, silky needles, but from cold ethylic acetate or chloroform in short, compact, transparent prisms; it is less readily soluble than the above-described dichloro-compound in the ordinary organic solvents. It melts at 152—153°, sublimes readily, and slowly volatilises in steam; when quickly heated under atmospheric pressure, a large proportion distils unchanged, but the distillate is of a dark colour.

The specific rotatory power of a chloroform solution containing 0·9800 gram in 25 c.c. was determined in a 2 decimetre tube at 13°; the mean of eight concordant readings gave $\alpha_D = +7° 45'$ whence $[\alpha]_D = +98·85°$.

The cold ethylic acetate solution, on spontaneous evaporation, deposits highly lustrous, stout prisms, which can readily be grown of a centimetre or so in length. If the crystals are deposited slowly from the cold solution, they are usually very transparent and show no trace of internal striæ; if they separate rapidly they are found to be considerably elongated in the direction of the *c*-axis, and are quite opaque, owing to the development of a fibrous internal structure.

Fig. 4.



The crystals belong to the orthorhombic system, although, owing to the absence of pyramid faces, it is impossible to say whether they are hemihedral or not. The prism forms *m*{110} and *n*{130} are usually the largest present, whilst the pinacoids *a*{100} and *b*{010}, which are so conspicuous on crystals of the corresponding dichloro-derivative, are usually small and frequently absent; the dome forms *r*{101} and *l*{011} are generally large and well-developed. All the forms give very fair reflections on the goniometer, although the crystals are rarely so suitable for measurement as those of *απ*-dichlorocamphor.

Crystalline System: Orthorhombic.

$a:b:c = 0·6860:1:0·3323.$

Forms present:—

a	{100}	$\infty\breve{P}\infty$
b	{010}	$\infty\bar{P}\infty$
c	{001}	0P
m	{110}	∞P
n	{130}	$\infty\bar{P}3$
l	{011}	$\bar{P}\infty$
r	{101}	$\breve{P}\infty$

The following angular measurements were obtained:—

	Angles.	No. of observations	Limits.	Mean.	Calculated.
nb	= 130 : 010	12	25° 51′—26° 1′	25° 57′	25° 55′
nn	= 130 : $\bar{1}$30	5	51 39—51 58	51 47	51 50
mn	= 110 : 130	15	29 26—29 45	29 36	29 38
an	= 100 : 130	3	64 0—64 12	64 7	64 5
mm	= 110 · 1$\bar{1}$0	13	68 40—69 7	68 53	68 52
am	= 100 . 110	5	34 18—34 31	34 24	34 26
bm	= 010 : 110	23	55 27—55 39	55 33	—
bl	= 010 : 011	18	71 34—71 41	71 37	—
ll	= 011 : 0$\bar{1}$1	9	36 40—36 53	36 46	36 46
cl	= 001 : 011	3	18 16—18 32	18 19	18 23
ar	= 100 : 101	5	64 1—64 18	64 12	64 9
cr	= 001 . 101	8	25 40—26 3	25 53	25 51
rr	= 101 : $\bar{1}$01	2	51 34—51 56	51 45	51 42

$\alpha\pi$-Chlorobromocamphor, $C_{10}H_{14}ClBrO$.

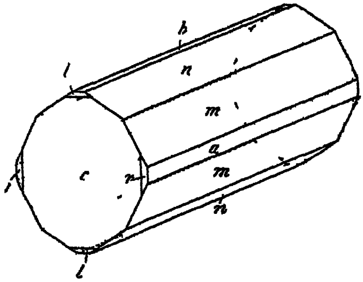
The preparation of this substance needs little description; on heating pure α-chlorocamphorsulphonic bromide in quantities of about 5 grams at a time at about 150° rapid effervescence sets in, and $\alpha\pi$-chlorobromocamphor sublimes in large quantities, being deposited on the cooler parts of the beaker in beautiful fern-like crystals; after about five minutes heating the operation is at an end.

The product is easily purified by recrystallisation from hot alcohol and ethylic acetate successively, and the yield is practically a theoretical one, 5 grams of the sulphonic bromide giving 3·8 grams of $\alpha\pi$-chlorobromocamphor. Two specimens obtained in different preparations gave satisfactory results on analysis.

0·1662 gave 0·2756 CO_2 and 0·0823 H_2O. C = 45·22; H = 5 5.
0·1675 „ 0·2764 „ 0 0792 „ C = 45 00; H = 5·25.
Theory: $C_{10}H_{14}ClBrO$ requires C = 45·2; H = 5·27 per cent.

$\alpha\pi$-Chlorobromocamphor crystallises from hot alcohol or acetic acid in long, flattened needles, and from cold ethylic acetate in beautiful, transparent prisms (Fig. 5); it resembles the dichloro- and dibromo-derivatives in its behaviour with most of the ordinary solvents, and is a very well characterised substance in all respects. It melts at 138—138·5°, almost the mean of the melting points of the dibromo- and

FIG. 5.



dichloro-compounds, and its melting point does not change on recrystallisation from acetic acid or other solvents.

A chloroform solution containing 1·6790 grams in 25 c.c. gave a rotation $\alpha_D = +11° 27'$ in a decimetre tube at 14° as the average of 10 observations; the specific rotation is therefore $[\alpha]_D = +85·24°$.

The crystals deposited by spontaneous evaporation of the ethylic acetate solution closely resemble those of $\alpha\pi$-dibromocamphor both in habit and appearance, and differ from them only by possessing somewhat less lustre.

Crystalline System: Orthorhombic.

$a : b : c = 0·6884 : 1 : 0·3301.$

Forms present:—

a	{100}	$\infty\breve{P}\infty$
b	{010}	$\infty\bar{P}\infty$
c	{001}	$0P$
m	{110}	∞P
n	{130}	$\infty\bar{P}3$
l	{011}	$\bar{P}\infty$
r	{101}	$\breve{P}\infty$

The following angular measurements were obtained.

Angle.	No. of observations.	Limits.	Mean.	Calculated.
nb = 130 : 010	16	25° 39′—25° 57′	25° 47′	25° 50′
nn = $\bar{1}30$: 130	5	51 31—51 49	51 38	51 40
mn = 110 : 130	18	29 20—29 58	29 35	29 37
an = 100 : 130	7	64 0—64 28	64 12	64 10
am = 100 : 110	12	34 23—34 39	34 30	34 33
bm = 010 : 110	15	55 16—55 30	55 25	55 27
bl = 010 : 011	26	71 31—71 56	71 44	—
ll = 011 : $0\bar{1}1$	11	36 24—36 37	36 30	36 32
cl = 001 : 011	17	18 1—18 39	18 16	18 16
ar = 100 : 101	28	64 11—64 35	64 23	—
cr = 001 : 101	12	25 19—26 1	25 42	25 37
rr = 101 : $\bar{1}01$	9	51 2—51 29	51 14	51 14

$\alpha\pi$-Bromochlorocamphor, $C_{10}H_{14}BrClO$.

The great difference between the sulphonic chlorides and the sulphonic bromides as regards their decomposition has already been alluded to, but the best example of this difference is afforded by a comparison of the behaviour of α-bromocamphorsulphonic chloride with that of α-chlorocamphorsulphonic bromide; whereas the latter undergoes decomposition very readily at about 150°, and gives an almost theoretical yield of $\alpha\pi$-chlorobromocamphor, its isomeride does not begin to decompose until the temperature has risen to about 170°, and the action which then occurs is apparently very complex, considerable quantities of hydrogen chloride or bromide being evolved together with sulphur dioxide and hydrogen sulphide, and a large proportion of carbonaceous matter being formed.

When the tarry mass obtained by heating the sulphonic chloride at about 180—190° for some time is subjected to distillation in steam, comparatively small quantities of a yellow oil, and, later on, a crystalline solid, pass over; after a time the oil solidifies, and the whole may then be separated by filtration. On repeatedly recrystallising this product from hot dilute alcohol and light petroleum, it was finally obtained in long, colourless needles, which melted, apparently quite sharply, at 142—143°, and which were so similar in appearance to the crystals of *aπ*-chlorobromocamphor that it was impossible to distinguish between them by ordinary methods. The analysis, however, did not give the calculated results, the percentage of carbon varying from 41·9 to 42·2, and that of hydrogen from 4·9 to 5·0, whereas a bromochlorocamphor contains 45·2 and 5·27 per cent. respectively; for this reason, we refrained from asserting in our first note (Proc., No. 124, 130) that this product was a bromochlorocamphor. Further investigation having shown that the substance was in reality a mixture, and all attempts to separate its constituents having failed, the decomposition of *α*-bromocamphorsulphonic chloride under various conditions was carefully studied. By varying the temperature at which the decomposition was carried out and the duration of the heating, products of very variable character were obtained; some of these, in fact, on repeated fractional crystallisation from alcohol, ethylic acetate, and other solvents, yielded fractions melting at temperatures ranging from about 120—150° (the most soluble portions melting almost sharply at 120°, the least soluble at 147—149°), but in no case could a definite product be isolated. The decomposition of the sulphonic chloride was then carried out under other conditions; in some experiments, iron filings were added, as their presence seemed to accelerate the decomposition, or the heating was carried out under greatly reduced pressure; in others, the sulphonic chloride was heated in boiling nitrobenzene solution. The products from these, as from previous experiments, crystallised readily in long needles, but were not homogeneous, and failed to yield a definite compound when subjected to repeated fractional crystallisation or fractional distillation in steam.

As it had been observed that the evolution of hydrogen chloride or bromide during the decomposition of the sulphonic chloride, and the darkening of the oil, were least noticeable during the first stages of the decomposition, a large quantity of the sulphonic chloride was carefully heated, in portions of about 2 grams at a time, the operation being continued only until the substance began to darken; the product, which contained a large quantity of unaltered sulphonic chloride, was now subjected to steam distillation, and the crystalline substance which collected in the distillate gently warmed with dilute alcoholic potash, to decompose any sulphonic chloride which had passed over. Two experiments, made in this way, gave a substance which crystallised from ethylic acetate in beautiful, transparent prisms, and which, in both cases, melted sharply at 132—133°; as all the mother liquors also gave crystals melting at 132—133°, it appeared probable that these products consisted of pure $\alpha\pi$-bromochlorocamphor. Analyses gave the following results.

$$\left.\begin{array}{l} C = 44{\cdot}3;\ H = 5{\cdot}84 \\ C = 44{\cdot}4;\ H = 5{\cdot}86 \end{array}\right\}\text{Theory: } C = 45{\cdot}3;\ H = 5{\cdot}3 \text{ per cent.}$$

As the analyses did not agree very satisfactorily with the calculated results, a further investigation of the substance was made, the results of which showed it to be a mixture; although on recrystallisation from alcohol four times, its melting point did not change, four crystallisations from acetic acid yielded a small fraction melting, not quite sharply, at 136—137°. This product, therefore, although certainly much less impure than that obtained in other ways, still contained a certain quantity of some compound from which experience had shown it could not be easily separated. For this reason, further attempts to prepare a pure $\alpha\pi$-bromochlorocamphor, isomeric with the compound already described, were not made.

The rotatory power of the impure compound in question was, however, determined, in order to make a rough comparison with that of the isomeride: 1·4658 grams dissolved in chloroform, and made up to 25 c.c., gave a rotation of $\alpha_D = +12° \ 36\frac{1}{2}'$ in a 2 decimetre tube at 13°, whence the specific rotation $[\alpha]_D = +107{\cdot}52°$.

The specific rotation is therefore +107°, whereas that of the isomeride is +85°; this great difference can hardly be due to the impurity present in the one bromochlorocamphor, and affords evidence of the non-identity of the two compounds. The nature of the substance which is present in the $\alpha\pi$-bromochloro-compound is unknown, but, as far as can be ascertained, it is the $\alpha\pi$-dibromocamphor melting at 152—153°; this is probable, from the fact that the melting point of some of the fractions rises to 147—149°, from the results of numerous combustions and halogen determinations, and from the great difficulty experienced in separating the impurity by fractional crystallisation; the two substances are isomorphous, and hence they crystallise together, giving crystals which appear to be those of a definite substance. The crystals obtained from various preparations, though having different melting points, give excellent results on goniometrical examination, no multiple images being obtained, as would be expected from ordinary impure substances.

Some of the crystals of the product melting at 132—133°, obtained from ethylic acetate solution, were examined, and found to belong to the orthorhombic system, and to exhibit the same forms as the preceding *aπ*-di-derivatives. The faces of the various forms are developed to about the same comparative sizes as those of the crystals of *aπ*-dibromocamphor, which they greatly resemble in appearance.

Crystalline System: Orthorhombic.

$a : b : c = 0{\cdot}6861 : 1 : 0{\cdot}3317.$

Forms present:—

a	{100}	$\infty\breve{P}\infty$
b	{010}	$\infty\bar{P}\infty$
c	{001}	$0P$
m	{110}	∞P
n	{130}	$\infty\bar{P}3$
l	{011}	$\bar{P}\infty$
r	{101}	$\breve{P}\infty$

The following angular measurements were obtained.

Angles.		No. of observations.	Limits.	Mean.	Calculated.
nb	= 130 : 010	12	25° 41′—26° 8′	25° 54′	25° 55′
nn	= 130 : $\bar{1}30$	7	51 43—51 57	51 50	51 49
mn	= 110 : 130	14	29 20—29 48	29 30	29 28
an	= 100 : 130	4	64 1—64 18	64 7	64 5
mm	= 110 : $1\bar{1}0$	8	55 24—55 41	55 34	55 32
am	= 100 : 110	18	34 19—34 45	34 27	34 27
bm	= 010 : 110	5	55 12—55 39	55 26	55 23
bl	= 010 : 011	29	71 24—71 56	71 39	—
ll	= 011 : $0\bar{1}1$	16	36 24—37 1	36 40	36 42
cl	= 001 : 011	9	18 0—18 41	18 19	18 21
ar	= 100 : 101	24	63 58—64 29	64 12	—
cr	= 001 : 101	12	25 31—26 7	25 46	25 48

The proportion of impurity present in this sample of *aπ*-chlorobromocamphor, judging from the analytical results, is small, and, as stated above, it is, in all probability, the isomorphous *aπ*-dibromocamphor; from the close approximation of the axial ratios of *aπ*-chlorobromocamphor and of the corresponding dibromo-derivative, it is evident that such an impurity could affect the axial ratios of the substance but slightly, since the axial ratios of an isomorphous mixture lie between those of its constituents, and are proportional to the amounts of each present. We therefore consider that the goniometric measurements made on this slightly impure sample of *απ*-bromochlorocamphor give very nearly the true axial ratios of the substance.

It is evident that the four new *απ*-dihalogen derivatives form a very well-defined isomorphous series, the axial ratios of the various members of which approximate very closely to each other, as shown in the following table.

Substance.	*a* : *b* : *c*.	*a* : *c* : *b*.
απ-dichloro-	0·6933 : 1 : 0·3297	2·1029 : 1 : 3·0331
απ-chlorobromo-..	0·6884 : 1 : 0·3301	2·0856 : 1 : 3·0296
απ-bromochloro-..	0·6861 : 1 : 0·3317	2·0684 : 1 : 3·0149
απ-dibromo-	0·6860 : 1 : 0·3323	2·0642 : 1 : 3·0090

The variation in dimensions in passing from one member of the series to another, is shown in the best possible manner by the following table of the principal angles lying in the three planes of symmetry.

	Angles.		
Substance.	*am* = 100 110.	*bl* = 010 : 011.	*ar* = 100 : 101.
απ-dichloro-....	34° 44′	71° 45′	64° 34′
απ-chlorobromo-	34 33	71 44	64 23
απ-bromochloro-	34 27	71 39	64 12
απ-dibromo-....	34 26	71 37	64 9

These two tables show that the axial ratios and principal angles of *απ*-chlorobromocamphor approximate very much more closely to those of *απ*-dichlorocamphor than do those of *απ*-bromochlorocamphor. It would seem, further, from a comparison of the dimensions of the two chlorobromo-compounds with those of the dibromo- and dichloro-derivatives, that the axial ratios are determined by the halogen atom occupying the *α*-position to a greater extent than by that which occupies the *π*-position.

The changes in values of the ratios a/b and c/b during the passage from one member of the series to another are in reverse directions but, within the limits of experimental error, of the same magnitude, so that the quantity $\frac{a}{b} \times \frac{c}{b}$ is approximately constant. It is evident that the *απ*-dihalogen derivatives differ in this respect from the previously measured dihalogen derivatives of camphor, for, as we pointed out in an earlier paper (Trans., 1893, **63**, 597), in the isomorphous series formed by these compounds, the comparative lengths of one pair of axes (a/b) are almost constant, whilst those of the other pair (c/b) change considerably during the passage from one member of the series to another.

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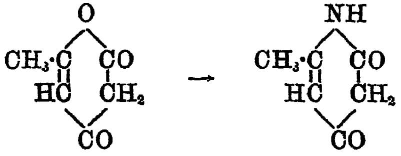
XLIV.—*Some Oxypyridine Derivatives.*

By Miss A. P. Sedgwick and N. Collie, F.R.S.E.

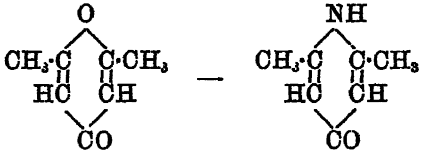
Amongst the many reactions of dehydracetic acid and its derivatives, those which yield pyridine derivatives are not the least interesting; moreover, as the change is easily effected by merely heating with strong ammonia, it is one which is not difficult to follow, and consequently the constitutional formulæ of the resulting nitrogen compounds are known with a considerable amount of certainty.

For instance, when the lactone of triacetic acid is treated with strong ammonia, the oxygen atom which closes the chain is replaced by the imido-group NH—



and a dioxypicoline is formed.

Similarly when dimethylpyrone is heated with ammonia—



the corresponding pyridine derivative, namely, lutidone, is produced. These two substances have constituted the material from which we have prepared a series of chloro- and oxy-pyridine compounds.

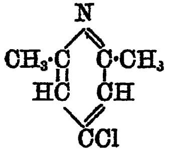
The original object of the research was to produce as many different oxypyridine derivatives of known composition as possible; for they are substances which possess most characteristic properties and reactions. Some give well-marked colorations with ferric chloride, such as the pyridine derivatives obtained from meconic acid which give blue or carmine red; others, like pyromekazone, resemble quinone in their properties, colouring the skin, and possessing a characteristic odour, &c., whilst the compound quinhydroketopyridine, obtained by Sell and Easterfield (Trans., 1893, **63**, 1047) from citrazinic acid is of a deep blue with metallic lustre.

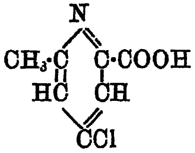
The introduction of extra hydroxyl groups into the pyridine ring, however, proved to be more difficult than we imagined, so we have at present contented ourselves with the preparation of various chloro-

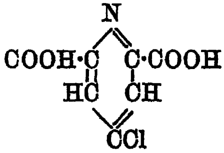
and oxy-acids which could be obtained from lutidone and dioxypicoline.

The chlorinated derivatives were easily prepared by the action of phosphorus halides on the oxy-compounds, and they are substances which, like the pyridine bases themselves, can be converted into pyridine acids when the alkyl groups, which are united to the pyridine ring, are oxidised by boiling with potassium permanganate solution.

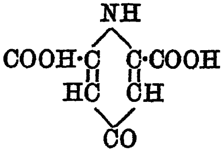
For instance, lutidone was first converted into monochlorolutidine, which in its turn was oxidised to a mono- and a di-carboxylic acid.



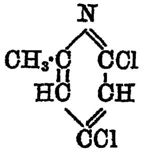


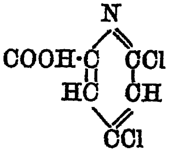


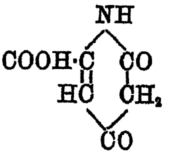
The dicarboxylic acid, on careful fusion with potash, yielded *chelidamic acid*—



an acid which was first obtained by the action of ammonia on chelidonic acid. The mono-acid, when heated, gave γ-chloropicoline. Proceeding in the same manner with dioxypicoline, chloro- and oxypicolinic acids were also obtained.

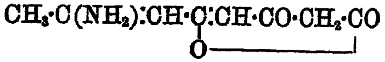






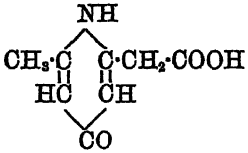
Preparation of γ-Chlor-αα′-dimethylpyridine.

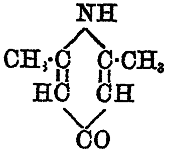
When solid dehydracetic acid is treated with strong ammonia solution, combination occurs, and an amido-compound is formed (Trans., 1893, 63, 128),



$$CH_3\cdot C(NH_2)\colon CH\cdot \underset{O}{\underset{|}{C}}\colon CH\cdot CO\cdot CH_2\cdot CO$$

which crystallises in long, silky needles. If, however, this substance is heated with more ammonia in a sealed tube at about 130° for several hours, it is gradually changed, and when the tube, on cooling, is no longer filled with silky needles, but with short, transparent crystals, the action is complete, and the dehydracetic acid is quantitatively converted into a mixture of lutidone and ammonium lutidonemonocarboxylate (Haitinger, *Ber.*, 1885, 18, 452).





These two substances can be easily separated by acidifying with sufficient hydrochloric acid to precipitate the free acid which is not very soluble in water, whilst the lutidone can be recovered from the filtrate. By this process, about 100 grams of lutidone and 25 grams of the free acid were obtained. Lutidonecarboxylic acid, when heated, can be quantitatively converted into lutidone, but as this acid was required for the preparation of some other pyridine derivatives described later on in this paper, it was kept for that purpose.

When lutidone is treated with phosphorus pentachloride, it is at once converted into γ-chlor-αα′-dimethylpyridine; but it is best to moderate the action by the addition of phosphorus oxychloride. Accordingly, 25 grams of lutidone were mixed with 20 grams of phosphorus oxychloride, and 40 grams of phosphorus pentachloride were slowly added to the mixture, keeping the temperature at about 140°.

The contents of the flask were then poured into water, and the volatile chloride distilled with steam. The yield is quantitative, and from 62 grams of lutidone, 70 grams of chloride were obtained; the theoretical amount is 71 grams. The boiling point of the pure chloride is 178° (corr.).

The oxidation of the γ-chlor-αα′-dimethylpyridine is best effected by boiling it with a dilute solution of potassium permanganate. Not more than 10 grams of the chloride were used in each experiment, and the theoretical quantity of permanganate necessary to oxidise the two methyl groups (23 grams) was always employed; the permanganate being added little by little to the boiling mixture of the chloride and 300—400 c.c. of water. After the whole of the permanganate had been converted into peroxide of manganese, usually about 3 grams of undecomposed chloride remained, which was recovered by distillation. The residue was filtered, and the filtrate, after evaporation, yielded a solid residue consisting of the potassium salts of a mono- and a di-carboxylic acid. In this way, 80 grams of the chloride were oxidised in 10 separate oxidations. The average yield of potassium salts for each experiment was 15 grams.

A partial separation was effected by merely adding hydrochloric acid to a solution of the crude potassium salts in water, when most of the insoluble acid separated; on standing over night, a large quantity of the second or more soluble acid separated in the crystalline form. The filtrate was then evaporated to dryness with excess of hydrochloric acid, and the residue extracted with alcohol; the alcoholic extract, after evaporation, yielded a further quantity of the soluble acid.

The mother liquors from the two acids still contained a small quantity of some substance which did not crystallise easily, but dried up to a semi-crystalline gum when left over sulphuric acid. On being distilled, it evolved carbon dioxide, and gave an oil smelling of chloropyridine; this was dissolved in hydrochloric acid and converted into the platinochloride.

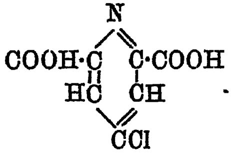
The salt contained no water of crystallisation, and, on analysis,

0·127 gave 0·0405 Pt; Pt = 31·5

$(C_5NH_4Cl)_4,2HPtCl_6$ requires Pt = 30·7 per cent.

The substance may, therefore, have contained γ-chloropyridinemonocarboxylic acid, but the quantity formed was too small to investigate.

γ-Chlor-αα'-pyridinedicarboxylic acid,



The less soluble acid seemed to be formed in greater quantity than the soluble one, and was first investigated. It is nearly insoluble both in hot and cold water, and was recrystallised from strong acetic acid. It forms granular crystals which decompose at about 220° with considerable charring.

0·4825 lost 0·042 when heated at 135°. H_2O = 8·7.

0·2410 gave 0·3440 CO_2 and 0·0705 H_2O. C = 38·9; H_2O = 3·2.

$C_5NH_2Cl(COOH)_2,H_2O$ requires C = 38·3; H = 2·7; H_2O = 8·2 per cent.

By neutralisation with caustic soda, it was found to be a dibasic acid. In order to prepare the salts, the acid was dissolved in ammonia and the ammonium salt solution evaporated till there was no longer any smell of ammonia. *The barium salt* is precipitated in the form of small crystals when the ammonium salt is added to a solution of barium chloride. It is soluble in hot water but crystallises out again on cooling.

0·304, after drying at 115^c, gave 0·2055 $BaSO_4$. Ba = 39·7.

0·1585, ,, ,, ,, 0·1070 ,, Ba = 39·7.

0·1875, when heated at 115°, lost 0·0265. $H_2O = 14·1$.
$C_5NH_2Cl(COO)_2Ba$ requires 40·6 Ba. $C_5NH_2Cl(COO)_2Ba,3H_2O$ requires $H_2O = 13·8$ per cent.

The sodium salt was prepared by neutralising the acid with caustic soda. It is very soluble in water, and only crystallises when evaporated to a syrup. Dried over sulphuric acid and then heated at 115°,

0·300 salt gave 0·175 Na_2SO_4. $Na = 18·9$.
$C_5NH_2Cl(COONa)_2$ requires $Na = 18·7$ per cent.

The following salts were prepared by double decomposition from the ammonium salt.

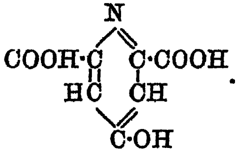
The silver salt, a white, gelatinous precipitate, unchanged by boiling.

The lead salt, a white precipitate which dissolves in hot water and crystallises out in needles on cooling.

The ferric salt, first a yellow colour is produced, which changes to a yellow precipitate.

The ferrous salt, even in dilute solutions a brilliant cherry-red colour is produced.

γ-Hydroxy-αα′-pyridinedicarboxylic acid or Chelidamic acid,



The first attempt to displace the chlorine in the γ-chlor-αα′-pyridinedicarboxylic acid by hydroxyl was by heating the acid with sodium ethoxide in a sealed tube; as the tube exploded, however, the acid was fused instead with 10 times its weight of caustic potash in a silver basin, only a gram of the acid being used for each operation. The product, when dissolved in water and acidified with hydrochloric acid, gave a granular precipitate; this was recrystallised from dilute alcohol, in which it was not very soluble. The crystals, when heated rapidly, do not melt properly, but at 255—260° decompose with copious evolution of carbon dioxide.

0·180 gave 0·305 CO_2 and 0·045 H_2O. $C = 46·2$; $H = 2·7$.
$C_5NH_2(OH)(COOH)_2$ requires $C = 45·9$; $H = 2·7$ per cent.

The ammonium salt crystallises only from concentrated solution.

Ferrous and ferric salts are both soluble, and form reddish-yellow solutions.

The silver salt is an insoluble gelatinous precipitate.

0·2605, dried at 115°, gave 0·1415 Ag. $Ag = 54·3$.
$C_7NH_3O_5Ag$ requires $Ag = 54·4$ per cent.

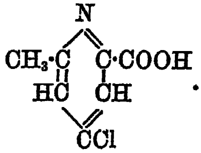
When the silver salt is heated, it behaves in a very characteristic manner; at a certain temperature it suddenly decomposes, and as the decomposition runs through the mass it swells up, forming a black residue, which at once begins to glow, and finally, without further heating, the glow gradually passes down to the bottom of the crucible, leaving a white mass of metallic silver.

This hydroxy-acid, also, when treated with bromine, gave a brominated acid, which coloured ferric chloride solution of a dirty purple.

From all these properties, the acid is evidently identical with *Chelidamic acid*, which was obtained by Lietzenmayer (*Inaug. Diss.*, Erlangen, 1878) by the action of ammonia on chelidonic acid.

According to Haitinger and Lieben (*Monatsh.*, 1885, **6**, 279), when chelidamic acid is heated to 250° it loses carbon dioxide and leaves γ-hydroxypyridine, which, after recrystallisation from water, melts at 66°, but when dry melts at 148°. Some of the γ-hydroxy-*αα'*-pyridinedicarboxylic acid was therefore heated in a distilling flask; the distillate was crystalline and melted at 140°. After dissolving in water, long needle-shaped crystals were obtained from the concentrated solution, and these melted at 66°, but at 145° when dry. The substance is, therefore, without doubt, γ-hydroxypyridine, and is of interest, as it has been prepared not only from chelidonic acid but also by Ost from comanic acid, which he had obtained from meconic acid (*Ber.*, 1884, **17**, R. 170).

αγ-Methylchloro-α'-pyridinecarboxylic acid,



After the insoluble acid had been separated from the products of oxidation of γ-chlorolutidine, a more soluble acid remained, which was purified by recrystallisation from water. It crystallises in small, needle-shaped crystals, which melt at 93—94°, and are soluble both in alcohol and in ether.

0·2005 (dried in a vacuum over sulphuric acid) gave 0·3425 CO_2 and 0·075 H_2O. C = 46·6; H = 4·1.

0·202, dried at 120°, lost 0·010 H_2O. H_2O = 4·9.

$C_7NH_6O_2Cl,\frac{1}{2}H_2O$ requires C = 46·5; H = 3 9; H_2O = 4·9 per cent.

The acid was also titrated with soda solution.

0·426 of acid neutralised 22·8 c.c. N/10 × 1·0249 soda solution.

$C_7NH_6O_2Cl,\frac{1}{2}H_2O$ requires 23·0 c.c. soda solution.

It is therefore a monobasic acid.

The following salts were prepared from the sodium salt by double decomposition.

Barium salt.—Immediate white precipitate. On warming it dissolves, but crystallises out again on cooling.

Heated to 105°, the salt turned red, and a smell of chloropicoline was noticed.

0·3219 gave 0·1549 $BaSO_4$; Ba = 28·3.

$(C_7NH_5O_2Cl)_2Ba$ requires Ba = 28·6 per cent.

Silver Salt.—White precipitate, insoluble in hot water.

Lead Salt—Immediate white precipitate, which mostly dissolves on heating, but, on cooling, crystallises out again in small nodules.

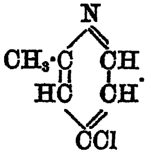
Copper Salt.—In neutral solution there is no precipitate at first, but soon a pale blue precipitate separates, which does not dissolve on warming.

Ferric Salt—A buff precipitate, which dissolves in excess of ferric chloride forming an orange solution.

Ferrous Salt.—An orange coloration.

The action of bromine on the acid was also tried. 2 grams of the acid were dissolved in glacial acetic acid, and 2 grams of bromine added; almost immediately lemon-yellow leaflets began to form; these were recrystallised from glacial acetic acid, and dried over sulphuric acid. When heated they gave off bromine, and, on analysis, they were found to contain 49·6 per cent. ClBr. $C_7H_5NO_2ClBr$ requires Cl,Br = 46·1 per cent. Probably, therefore, a small quantity of a bromine additive product had been formed as well as the substitution compound.

αγ-Methylchloropyridine,



When the acid melting at 93° is heated in small quantities in a test tube, carbon dioxide is evolved, charring takes place, and red vapours, together with an oil and a small quantity of crystalline distillate volatilise into the upper portion of the tube. A strong smell of chloropicoline was also noticed. About 5 grams were treated in this way in a large number of test tubes, which were then washed out with dilute hydrochloric acid. The solution thus obtained was made alkaline with soda, and steam blown through it; the distillate contained the chloropicoline which, after purification, boiled at 162·5° —163·5° (corr.).

0·113 gave 0·235 CO_2 and 0·048 H_2O. C = 56·7; H = 4·7.

$C_5NH_3(CH_3)Cl$ requires C = 56·5; H = 4·7 per cent.

The platinochloride is a yellow, crystalline substance, and can be recrystallised from hydrochloric acid.

0·231 gave 0·0675 Pt. Pt = 29·4.

$[C_5NH_3(CH_3)Cl]_2,H_2PtCl_6$ requires Pt = 29·3 per cent.

A chloropicoline has been noticed by Ost (*Ber.*, 1883, **16**, R. 1374), who obtained it by reducing penta- and hexa-α-chloropicoline with tin and hydrochloric acid. He gives its boiling point as 164—165°; possibly this substance is identical with the γ-chloropicoline we have prepared.

A further experiment was tried to see if the yield of chloropicoline, could be improved by heating the acid melting at 93° in an oil bath, and during the decomposition passing a stream of carbon dioxide through the apparatus. The yield, however, was not in any way better than that obtained by heating the acid rapidly in small quantities in test tubes. From about 15 grams of the acid, only 1·5 grams of chloropicoline were obtained.

Some γ-chloropicoline was boiled from 3 to 4 hours with a solution of potassium permanganate; it was thus oxidised to the potassium salt of γ-chloro-α-picolinic acid. The potassium salt was purified by recrystallisation and analysed.

0·234 gave 0·105 K_2SO_4 = 20·4 K.

$C_5H_3NCl{\cdot}COOK$ requires K = 19·9 per cent.

The free acid was recrystallised from water. It melts at 194—195° (corr.), and begins to blacken at 185°.

The following salts were prepared from a neutral and moderately concentrated solution of the ammonium salt.

Silver Salt.—A white flocculent precipitate which, when warmed, turns to a mass of felted needles.

Lead Salt.—A white precipitate, soluble in hot water, but separates out again on cooling in a non-crystalline condition.

Copper Salt.—Blue precipitate, insoluble in hot water, but turns slightly pink.

Zinc Salt.—A crystalline, granular precipitate.

Barium Salt.—Small, transparent crystals separate out of the solution.

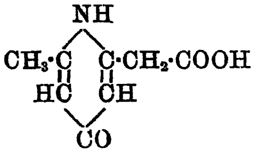
A small quantity of the acid was fused with caustic potash; and from the fused mass an acid was obtained which, after recrystallisation from water formed bunches of small rectangular or square plates. The melting point, after four recrystallisations, remained constant at 263—264° (or 275—276° corr.). They did not contain chlorine. Possibly this acid is identical with an oxypicolinic acid melting at 258°, obtained by Bellman (*Ber.*, 1884, **17**, 106) by reducing monochloro-γ-(?)-oxypicolinic acid with tin and hydrochloric acid.

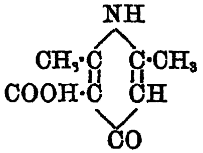
The ammonium salt of γ-chloropicolinic acid gave, with *silver nitrate*, a precipitate which was soluble in hot water, but crystallised out again on cooling.

Ferric Salt.—An orange precipitate.

Copper Salt.—A blue precipitate.

In the preparation of lutidone, mentioned a few pages back (p. 401), another compound, lutidonemonocarboxylic acid was also produced; its formula is not known with certainty, but if that which one of us (Trans., 1891, 59, 183) has suggested for dehydracetic acid be correct, then it must be the first of the two following.

I. 

II. 

This substance, when treated with pentachloride of phosphorus, yields a chlorinated acid; 21 grams of the acid were mixed with excess of phosphorus oxychloride and 25 grams of pentachloride of phosphorus added gradually; the temperature of the mixture being finally raised to 160°. There was no violent action; and the residue when added to water, neutralised with soda and boiled, yielded a small quantity of some volatile chloride which distilled over. The solution was then evaporated to dryness with excess of hydrochloric acid, and extracted with alcohol; the crystals obtained from the alcoholic solution were purified by recrystallisation from water. Their m. p. was 183° (corr.).

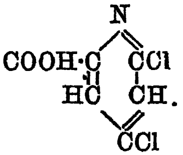
0·2318 lost 0·038 at 120°. $H_2O = 16·3$.
0 2112 gave 0·3385 CO_2 and 0·101 H_2O. $C = 43\ 7$; $H = 5·3$.
$C_8NH_8O_2Cl,2H_2O$ requires $C = 43·3$; $H = 5·4$; $H_2O = 16·2$ per cent.

The silver salt is precipitated when the ammonium salt is added to silver nitrate solution.

0 2005 gave 0·074 Ag (after ignition in hydrogen). $Ag = 36·9$.
$C_8NH_7ClO_2$ requires $Ag = 36\ 9$ per cent.

When this salt is heated, it decomposes violently with a series of small explosions, and leaves hardly a trace of silver chloride. Most of the salts of this acid are very soluble in water. A curious copper salt is formed when a solution of copper acetate is added to the ammonium salt of the acid; at first no change occurs, but on standing a brilliant purple copper salt is produced, which is quite insoluble in water.

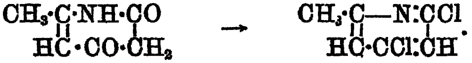
Preparation of the αγ-dichloropicolinic acid,



In a former paper (Collie and Myers, Trans., 1892, **61**, 721), it was shown how a dioxypicoline could be obtained by the action of strong ammonia on the lactone of triacetic acid,

$$C_6H_6O_3 + NH_3 = C_6H_7NO_2 + H_2O.$$

This compound when treated with oxychloride of phosphorus yields a dichloropicoline.



$$\begin{array}{l} CH_3\cdot \overset{}{C}\cdot NH\cdot CO \\ \quad\| \qquad\qquad | \\ \;HC\cdot CO\cdot CH_2 \end{array} \longrightarrow \begin{array}{l} CH_3\cdot C—N:CCl \\ \quad\| \qquad\qquad | \\ \;HC\cdot CCl:CH \end{array}.$$

When 30 grams of dioxypicoline are treated with about 70 grams of phosphorus oxychloride, and the temperature is not allowed to rise above 120°, the action is complete as soon as feathery crystals begin to sublime on to the neck of the flask; the yield of dichloropicoline is from 25—30 grams. The boiling point of the pure dichloride is 205—206 (corr.). When dichloropicoline is heated with a dilute solution of potassium permanganate, oxidation takes place slowly. Usually about 10 grams of the chloride were boiled with about 500 c.c. of water, and 20 grams of permanganate slowly added. When all the permanganate had been reduced, a certain quantity of undecomposed chloride was recovered by distillation; the peroxide of manganese was then removed by filtration, and from 9 to 10 grams of potassium salt of dichloropicolinic acid were obtained by evaporating the filtrate to dryness. In all, 35 grams of dichloropicoline gave 50 grams of the crude potassium salt. This salt when purified by recrystallisation was obtained in the form of fine silky needles.

In order to prepare the free acid, the potassium salt was dissolved in water and hydrochloric acid added, when the bulk of the dichloropicolinic acid crystallised out of the solution, and by evaporation a further quantity was obtained. It was purified by dissolving it in alcohol and adding water; it crystallises in long white needles which are soluble in alcohol but only sparingly so in water.

0·319 gave 0·436 CO_2 and 0·0565 H_2O; C = 37·5. H = 1·9.
0·158 „ 0·2355 AgCl; Cl = 36·5.
$C_6NH_3O_2Cl_2$ requires C = 37·5; H = 1·6. Cl = 36·9 per cent.

It melts at 101—102°. When heated rapidly in a test tube, both carbon dioxide and hydrogen chloride are evolved. The salts of dichloropicolinic acid were prepared from the ammonium salt by double decomposition.

Silver Salt.—Gelatinous precipitate insoluble in water and not changed by boiling.

Lead Salt.—White crystalline precipitate consisting of needles; partly soluble in hot water.

Mercuric Salt.—Soluble.

Ferric Salt.—Buff coloured precipitate.

Ferrous Salt.—Bright orange precipitate, which changes to orange-red crystals on standing.

Zinc Salt.—Separates in lozenge-shaped crystals from concentrated solutions on standing.

Calcium Salt.—Crystalline precipitate.

Magnesium Salt.—Soluble.

The Barium Salt was prepared from the ammonium salt in the form of small crystals. These were recrystallised.

0·280 (air dried) gave 0·116 $BaSO_4$. Ba = 24·4.

0·108 lost at 110. 0·0085 H_2O = 7·8.

$(C_6NH_2O_2Cl_2)_2Ba,2H_2O$ requires Ba = 24·6; H_2O = 6·8 per cent.

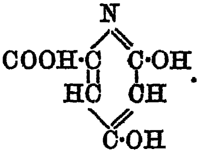
When dichloropicolinic acid is heated to 150—160°, it gives off a little water and the fused mass then becomes solid. This substance is insoluble in most reagents, but if dissolved in alcohol and water dichloropicolinic acid melting at 101° is again reproduced, and as dichloropicolinic acid does not contain water of crystallisation, the solid is probably an anhydride. If the acid, however, be heated above 170°, the solid again melts, carbon dioxide begins to come off and at 190° the mass turns green and then rapidly chars.

2·043 acid gave 0·461 CO_2. CO_2 = 22·5.

$C_6NH_3O_2Cl_2 = C_5NH_3Cl_3 + CO_2$ requires CO_2 = 22·8 per cent.

Attempts were made to obtain dichloropyridine from the charred residue, but without result.

αγ-Dioxypicolinic acid,



Diethoxypicolinic acid was first prepared by boiling the dichloropicolinic acid with sodium ethoxide for two days. The precipitated sodium chloride was then filtered off, and the alcoholic solution evaporated. On adding hydrochloric acid in very slight excess, an oil was precipitated which soon crystallised on standing. When purified by recrystallisation from alcohol and water, it melted at 93—95°.

The sodium salt was analysed.

0·140 gave 0·036 Na_2SO_4. Na = 8·3.

0·2505 lost at 120° 0·032 H_2O. H_2O = 12·7.

$C_{10}NH_{12}O_4Na,2H_2O$ requires Na = 8·5. H_2O = 13·3 per cent.

As there was only a very small quantity of diethoxypicolinic acid, it was all used in the preparation of dioxypicolinic acid. This change may be effected either by heating the ethoxy-acid in a sealed tube with hydriodic acid, or by boiling it with fuming hydriodic acid; by either process, a crystalline precipitate of dioxypicolinic acid is formed together with ethylic iodide. The acid is not very soluble in water, and was recrystallised from strong hydriodic acid. When pure, it melts at 260—263° (270—273° corr.) but begins to darken in colour at 240°; after melting, it chars and completely decomposes.

The ammonium salt gives, with ferric chloride, a yellow coloration, but none with ferrous sulphate. The silver salt was prepared from the ammonium salt by double decomposition; it is insoluble in water, and turns brown on heating or drying.

0·2125 (dried in a vacuum over sulphuric acid) gave 0·093 Ag. Ag = 43·7.

$C_5NH_2(OH)_2{\cdot}COOAg$ requires Ag = 42·8 per cent.

An analysis of the acid was also made.

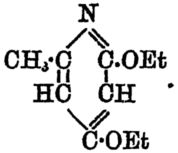
0·2205 (dried at 100°) gave 0·370 CO_2 and 0 0760 H_2O. C = 46 6; H = 3·8.

$C_6NH_5O_4$ requires C = 46·4; H = 3·2 per cent.

This acid is isomeric with another dioxypicolinic acid, comenamenic acid (obtained from meconic acid, Ost, *Ber.*, 1883, 16, 1373, and *Ber.*, 1884, **17**, R. 169), but, as the latter gives a splendid, purple-red coloration with ferric chloride, the dioxypicolinic acid we have obtained cannot be identical with it.

Several attempts were made to produce $\alpha\gamma$-dioxypyridine by fusing dioxypicolinic acid with potash, but they were not very successful. In one experiment a certain quantity of dioxypicolinic acid was recovered unchanged; in another, after fusion, the mass was dissolved in water, acidified with hydrochloric acid, and then extracted with ether. The ethereal extract, on evaporation, left a small, non-crystalline residue, which, with ferric chloride, gave a splendid, green colour, turning to blue. The aqueous solution, which had been extracted with ether, was evaporated to dryness and treated with absolute alcohol. The residue obtained from the alcoholic extract gave, with ferric chloride, a purple-violet coloration, very similar to that produced by pyrocomenamenic acid, $C_5NH_3(OH)_2$, but we were quite unable to separate any substance from the fused mass, even in sufficient quantity to make a melting-point determination.

αγ-Diethoxypicoline,

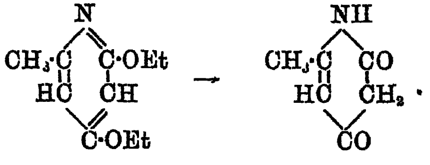


This substance can be easily prepared from dichloropicoline: 8 grams of dichloropicoline were treated in alcoholic solution with excess of sodium ethoxide (5 grams Na) and the mixture warmed, when a copious precipitate of sodium chloride formed at once, the action proceeding rapidly. After boiling for two hours, the salt was filtered off, and the alcoholic filtrate mixed with a little water, evaporated, and the residue extracted with ether. This ethereal solution yielded an oil of a pleasant, sweet smell, and boiling at 230—235° (238—243° corr.). The platinochloride was prepared and analysed.

0·1245 gave 0·0312 Pt. Pt = 25·1.

$[C_5NH_2Me(OEt)_2]_2,H_2PtCl_6$ requires Pt = 25·2 per cent.

This platinum salt, after purification, was decomposed by hydrogen sulphide, and from the filtrate pure diethoxypicoline was prepared; it boiled at 230—232° (238—240° corr.). It forms crystalline salts with acids. When heated in a sealed tube with hydriodic acid, crystals were obtained, which, after recrystallisation from alcohol and from water, proved to be regenerated dioxypicoline, melting at 310—315°. This experiment shows that, although diethoxypicoline is a true pyridine derivative, giving salts, &c., yet, on displacing the ethyl groups by hydrogen, the substance changes back again into the imido-ketonic form, which is almost devoid of basic properties.



An experiment was therefore tried to see whether the presence of a CO-group could be demonstrated by the action of phenylhydrazine: 2 grams of dioxypicoline and 6 grams of phenylhydrazine were heated in a sealed tube, and the crystalline product purified by crystallisation from alcohol.

0·1542 gave 25·8 c.c. N at 21° and 757 mm. N = 19·2.

$C_6NH_7O{:}N_2H{\cdot}C_6H_5$ requires N = 19·5 per cent.

The substance is, therefore, the hydrazide of a monoxypicoline. It is more probable that it is an α-oxy-γ-hydrazide of picoline than that the hydrazine residue is in the α-position. Dioxypicoline does not seem to react with hydroxylamine.

Several trials were also made to further chlorinate dichloropicoline. Chlorine was passed through an acetic acid solution of the substance, both at the ordinary temperature and at the boiling point, but scarcely any action occurred, and, although some hydrogen chloride was produced, it was found to be due to the formation of chloracetic acid. Even when chlorine was bubbled through boiling dichloropicoline itself, the action was only very slight; no definite compound was formed, even after several hours' action, and nearly all the dichloropicoline was recovered unchanged.

Having been unsuccessful in our attempts to obtain a trichloropicoline, we next tried the action of cold dilute solution of potassium permanganate on the dioxypicoline, hoping that possibly a trioxypicoline would be produced; 16 grams of dioxypicoline were shaken with dilute potassium permanganate solution, the mixture being kept cold; the colour of the permanganate disappeared almost the moment it was added. At the end of the action, the whole was gently heated on a water bath, filtered, and the filtrate evaporated with just sufficient hydrochloric acid to render it neutral; long, needle-shaped crystals were obtained, melting at 179° (corr.), the yield, however, was small. The substance, after recrystallisation from alcohol, did not give any characteristic coloration with ferric chloride, the liquid merely acquiring an orange tint.

0·1837 gave 0·341 CO_2 and 0·077 H_2O. C = 50·8; H = 4·7.
0·161 „ 13·6 c.c. moist nitrogen at 18 and 769 mm. N = 9·8.
$C_6NH_7O_3$ requires C = 51·1; H = 4·9; N = 9·8 per cent.

The substance may be a trioxypicoline, but, unfortunately, we were never able to exactly reproduce the exact conditions necessary for its formation. Many experiments were tried, but all without success.

In some of these experiments, on evaporating the filtrate from the precipitated manganese dioxide, a yellow compound was obtained, which, when recrystallised from alcohol, melted at 252° (262° corr.).

The mean of three analyses gave C = 51 9; H = 6·0 per cent.; it contained also N = 8·1 per cent. These numbers, however, do not seem to agree with those required by any simple oxidation product. The substance may not have been pure, but its melting point remained constant. We were not able, however, to further study the properties of this substance.

Dioxypicoline seems to remain unchanged when submitted to the action of reducing agents; sodium amalgam did not change it, and when heated in a sealed tube with fuming hydriodic acid and phosphorus, the compound either remained unchanged or it is completely decomposed, in one experiment with the formation of large quantities of phosphonium iodide, acetic acid, and carbon dioxide.

University College,
London.

XLV.—*The Colouring Principle of Toddalia aculeata and Evodia meliæfolia.*

By A. G. Perkin and J. J. Hummel.

Toddalia Aculeata.

This Indian plant, belonging to the *Rutaceæ*, is a rambling shrub found in the sub-tropical Himalayas, in the Khasia Mountains, and throughout the Western Peninsula, and Ceylon.

The root-bark is used in Madras as a yellow dyestuff, and it is also highly spoken of by various writers as one of the most valuable of Indian medicinal products, possessing tonic, stimulant, and antipyretic properties. It was introduced into European medicine in 1771, and at one time enjoyed some celebrity under the name of "Lopez Root," but it has long since fallen into disuse.

The toddalia root does not appear to have been ever satisfactorily examined. Flückiger and Hanbury state that they found the root-bark to contain an essential oil, and some substance, precipitated from the aqueous solution by tannic acid, which they regarded as an indifferent bitter principle rather than as an alkaloïd. They state that they were unable to detect the presence of berberine.

For the small sample examined by us, we are indebted to Dr. G. Watt, from whom it was obtained during his official connection with the Colonial and Indian Exhibition, London, 1886.

The root, about $\frac{3}{4}$ inch in diameter, possesses a marked aromatic odour, and has a pale yellowish, almost white, woody centre, and a brown bark covered with a bright yellow, soft, powdery, pith-like substance. The central woody portion, the inner bark, and the external yellow powder were separately examined.

Ten grams of the *external yellow powder* were digested for two hours with 100 c.c. of boiling alcohol, filtered, and the residue again treated in a similar manner. To the orange-brown filtrate alcoholic lead acetate solution was added drop by drop as long as a colourless precipitate was formed, and after this had been removed by filtration, the filtrate was evaporated to a small bulk and poured into five times its volume of dilute hydrochloric acid. A viscous, yellow precipitate was thus obtained, which increased in quantity on standing; this was collected upon calico, and, after being rinsed with cold, was digested with boiling water; the turbid, yellow liquid thus obtained contained resinous matter in suspension, but this was readily removed by means of ether. After boiling the clear aqueous solution, excess of hydrochloric acid was added, and on cooling, it deposited long, orange-coloured needles, which were collected and washed with dilute hydrochloric acid. To purify this product, it was dissolved in boiling dilute alkali and the solution digested with animal charcoal, filtered, treated with hydrochloric acid, and allowed to cool; the yellow needles which separated were collected, washed with water, and allowed to dry at the ordinary temperature. The product weighed 0·35 gram.

For analysis this was converted into the platinochloride in the usual manner, and the resulting amorphous, yellow powder dried at 100°.

0·294 on ignition yielded 0·0535 Pt. Pt = 18·19.

$(C_{20}H_{17}NO_4)_2,H_2PtCl_6$ requires Pt = 18·02 per cent.

The analytical numbers accorded therefore with those given by berberine platinochloride. Its identity with this substance was shown by a comparison of the reactions of the hydrochloride above referred to with berberine hydrochloride obtained from other sources.

The *inner bark* of this root (60 grams) was found, on examination by the above method, to contain but a trace of berberine, so small, indeed, that this was probably derived from traces of the preceding yellow powder still adhering to it. It contained, however, some quantity of a sticky, resinous product which was insoluble in water or dilute acids, but readily soluble in ether, and appeared to be identical with the similar substance present in the yellow powder. The quantity obtainable was too small for extended examination, and the preliminary experiments were not successful in extracting from it any crystalline substance. The *central woody portion* of the root yielded no berberine.

Evodia Meliæfolia.

This tree, belonging to the *Rutaceæ*, is found in China and Japan, where its bark is largely employed in dyeing as well as in medicine. It was formerly described by Loureiro and others as *Pterocarpus flavus*, but this error was eventually corrected by P. W. Squire (*Pharm. Jour.*, [3], 1888, **18**, 785), who proved it to be really *Evodia glauca*, which is synonymous with *E. meliæfolia* (*Flora, British India*, 1, 490). Some time ago we received from Mr. James

Buchanan, of Shanghai, a small sample of bark called by the Chinese "hwang-peti," exhibiting all the characteristics described by Squire, and its identity with that of *Evodia meliæfolia* having been determined for us by Mr. Thistleton Dyer, Director of the Royal Botanic Gardens, Kew, we examined it both chemically and tinctorially.

The literature of this dyestuff is extremely meagre, the only references to its colouring principle we have met with being those of G. Martin, Tokio (*Archiv. d. Pharm.*, 1878, **13**, 337), and of P. W. Squire (*loc. cit.*). The former merely states the fact that he found the bark to contain berberine, and the latter that the reactions of the aqueous decoction of the bark with picric acid, hydrochloric acid, and calcium hypochlorite indicated the presence of berberine. Neither of these observers furnish analytical data, and it appeared to us therefore desirable to obtain conclusive confirmation of these statements.

Fifty grams of the finely ground bark were extracted with alcohol, and the extract treated in a similar manner to that described under *Toddalia aculeata* (p. 413); a crystalline yellow product was obtained closely resembling berberine hydrochloride, and this was converted into the platinochloride, and dried at 100°.

0·4555 gave on ignition 0·0825 Pt. Pt = 18·11.

0·2404 „ 0·3907 CO_2 and 0·0760 H_2O. C = 44·32; H 3·51.

$(C_{20}H_{17}NO_4)_2,H_2PtCl_6$ requires C = 44·47; H = 3·33; Pt = 18·02 per cent.

It was evidently berberine platinochloride. This bark also contains some quantity of a resinous substance soluble in ether, apparently identical with that found in the *Toddalia aculeata*.

Having some quantity of the root of the *Coscinium fenestratum* which contains berberine (Perrins, *Annalen*, 83, 276), it was examined by the preceding method in the hope that it would contain sufficient of this resinous substance for examination. Berberine was readily obtained, though the resinous substance was found to be absent from the root.

Dyeing Properties.—A series of dyeing experiments were made with the evodia bark on silk, wool, and cotton. Wool and silk, without being mordanted, are readily dyed a bright yellow by boiling for half an hour in an aqueous decoction of the bark. The addition of 1 per cent. of sodium carbonate to the dye bath is beneficial by increasing the intensity of the colour without impairing its brilliancy. Larger additions of sodium carbonate give still deeper colours, but they are not so bright; prolonged boiling acts in the same direction. Evodia bark is best adapted for dyeing silk, on which a full, bright yellow is obtained with 20 per cent. of dyestuff.

Cotton has no attraction for the dye unless it has been previously mordanted with tannic acid, when it is dyed in neutral bath a dull yellow.

The foregoing experiments indicate that the bark contains a basic colouring matter which behaves in the normal manner. A comparative dyeing experiment on wool indicated that evodia bark contains the equivalent of 3 per cent. of berberine hydrochloride.

Experiments with toddalia gave similar results.

Clothworkers' Research Laboratory,
Dyeing Department, Yorkshire College.

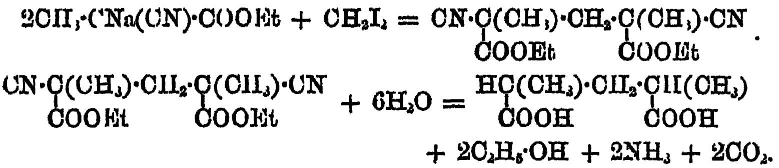
XLVI.—*Trimethylsuccinic and αα₁-Dimethylglutaric acids.*

By Wm. A. Bone, M.Sc., Ph.D. (late Fellow of Victoria University), and W. H. Perkin, jun., F.R.S.

Introduction.

During the last few years, there has been considerable discussion as to the conditions of formation and properties of the isomeric acids which form the subject matter of this communication, and in spite of a great deal of experimental work it is only quite recently that the various issues raised in the controversy have been at all clearly understood.

In 1889, Zelinsky (*Ber.*, 1889, **22**, 2823) first obtained a mixture of two isomeric $\alpha\alpha_1$-dimethylglutaric acids by acting on the sodium compound of ethylic α-cyanopropionate with methylenic iodide, and then hydrolysing the product and heating the acids thus obtained to 200°. The reactions involved in this process may be thus written.



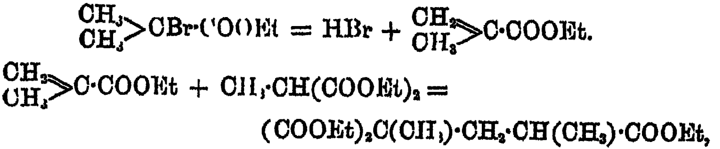
$$2CH_3\cdot CNa(CN)\cdot COOEt + CH_2I_2 = CN\cdot\underset{\text{COOEt}}{C}(CH_3)\cdot CH_2\cdot\underset{\text{COOEt}}{C}(CH_3)\cdot CN\ .$$

$$CN\cdot\underset{\text{COOEt}}{C}(CH_3)\cdot CH_2\cdot\underset{\text{COOEt}}{C}(CH_3)\cdot CN + 6H_2O = H\underset{\text{COOH}}{C}(CH_3)\cdot CH_2\cdot\underset{\text{COOH}}{CH}(CH_3) + 2C_2H_5\cdot OH + 2NH_3 + 2CO_2.$$

He separated the two isomeric acids by fractional crystallisation from a mixture of benzene and light petroleum. The more insoluble acid melted at 128° and the more soluble at 102° to 104°, but they resembled each other very closely in their other properties.

In the following year, Bischoff and Mintz (*Ber.*, 1890, **23**, 647) described as trimethylsuccinic acid an acid melting at 105°, and yielding an anhydride melting between 67° and 82°, which they had prepared from the product of the action of ethylic α-bromisobutyrate on an alcoholic solution of the sodium compound of ethylic methylmalonate. Shortly afterwards, Bischoff (*Ber.*, 1890, **23**, 1464) repeated Zelinsky's preparation of the $\alpha\alpha_1$-dimethylglutaric acids, and obtained an acid melting at 100—101°. He found its dissociation constant to be identical with that of the "trimethylsuccinic acid" prepared by himself and Mintz, namely $K = 0{\cdot}0054$. Despite this fact, he considered that the latter was a true trimethylsuccinic acid, mainly on account of its method of formation, as it was difficult to see how any acid other than trimethylsuccinic could be formed in this way. Auwers and Jackson (*Ber.*, 1890, **23**, 1599) argued from the smallness of its dissociation constant that Bischoff was mistaken in calling his acid "trimethylsuccinic acid," and that it was in reality a dimethylglutaric acid. Ostwald had shown that in the substituted succinic acids the dissociation constant increases in value with the number of alkyl groups, whereas the dissociation constant of Bischoff's acid is actually below that of succinic acid itself ($K = 0{\cdot}00665$). Further, the identity of its dissociation constant and that of Zelinsky's $\alpha\alpha_1$-dimethylglutaric acid, and the fact that when treated with bromine according to the Hell-Vollard-Zelinsky method it yielded the anhydride of a dibromo-acid, and therefore contained two α-hydrogen atoms, showed that in reality it was a dimethylglutaric acid. To explain its formation by the action of ethylic α-bromisobutyrate on the sodium compound of ethylic methylmalonate, Auwers supposed that under the conditions of the experiment the ethylic α-bromisobutyrate loses hydrogen bromide and yields ethylic methacrylate, this then condenses with the sodium compound of ethylic methylmalonate forming the ethylic salt of a tricarboxylic acid, which on subsequent hydrolysis and heating of the resulting acid to 200° would give $\alpha\alpha_1$-dimethylglutaric acid.*

The reactions which are supposed to occur may be thus expressed.



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CBr{\cdot}COOEt = HBr + \begin{matrix}CH_2\\CH_3\end{matrix}\!\!\gg C{\cdot}COOEt.$$

$$\begin{matrix}CH_2\\CH_3\end{matrix}\!\!\gg C{\cdot}COOEt + CH_3{\cdot}CH(COOEt)_2 = (COOEt)_2C(CH_3){\cdot}CH_2{\cdot}CH(CH_3){\cdot}COOEt,$$

and so on.

Bischoff (*Ber.*, 1891, **24**, 1041) then admitted the correctness of Auwer's explanation, but on further investigation he showed that if ethylic α-bromisobutyrate and the sodium compound of ethylic methylmalonate were allowed to interact in xylene at 180°, instead of in alcoholic solution, a mixture of ethereal salts was obtained which on hydrolysis yielded, besides the dimethylglutaric acid melting at 102° to 105°, a large quantity of an isomeric acid melting at 139·5°, and having a dissociation constant K = 0·0310, and which he therefore concluded was trimethylsuccinic acid.

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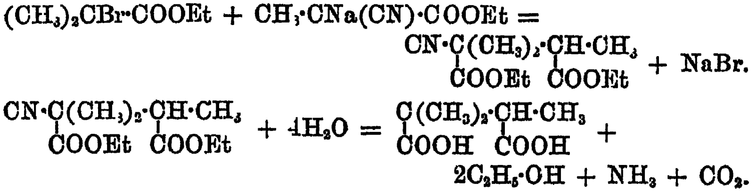
* We may here note that a very similar explanation was given by Hell of the fact that when ethylic α-bromisobutyrate is treated with molecular silver, and the product hydrolysed, a mixture of tetramethylsuccinic and trimethylglutaric acids is obtained (*Ber.*, 1890, **23**, 298).

Zelinsky (*Ber.*, 1891, **24**, 459) next prepared trimethylsuccinic acid by the action of ethylic α-bromisobutyrate on the sodium compound of ethylic cyanopropionate in alcoholic solution, subsequently hydrolysing the ethylic cyanotrimethylsuccinate thus formed with dilute sulphuric acid, and then heating the product at 200° until carbon dioxide ceased to be evolved.



$$(CH_3)_2CBr\cdot COOEt + CH_3\cdot CNa(CN)\cdot COOEt = CN\cdot\underset{COOEt}{C}(CH_3)_2\cdot\underset{COOEt}{CH}\cdot CH_3 + NaBr.$$

$$CN\cdot\underset{COOEt}{C}(CH_3)_2\cdot\underset{COOEt}{CH}\cdot CH_3 + 4H_2O = \underset{COOH}{C}(CH_3)_2\cdot\underset{COOH}{CH}\cdot CH_3 + 2C_2H_5\cdot OH + NH_3 + CO_2.$$

The product, however, was in reality a mixture; and by fractional crystallisation from a mixture of benzene and light petroleum he isolated two acids; the less soluble melting at 140—141° and having a dissociation constant K = 0·0322; the more soluble melting at 100—101° and having a dissociation constant K = 0·0063. He maintained that they were *both* trimethylsuccinic acids, and that the acid of lower melting point was quite distinct from the dimethylglutaric acid melting at about the same temperature.

Auwers (Auwers and Köbner, *Ber.*, 1891, **24**, 1923) strongly dissented from Zelinsky's view of the nature of his acid of lower melting point, and showed that its chemical and physical properties so closely resembled those of the dimethylglutaric acid melting at 105° that the two substances must be identical. Both acids when treated with acetyl chloride yielded the same anhydride melting at 95°, and this on treatment with water gave an acid melting at 128°, identical with the dimethylglutaric acid of higher melting point. Zelinsky, however, was unconvinced, and still remains so. Of course the formation of dimethylglutaric acid from ethylic cyanopropionate and ethylic bromisobutyrate is readily understood if it be assumed that the reaction takes place in a similar way to that by which Bischoff obtained dimethylglutaric acid from ethylic methylmalonate and ethylic α-bromisobutyrate (see p. 417).

In 1893, Koenigs (*Ber.*, 1893, **26**, 2337), by the oxidation of camphoric acid with chromic acid, obtained a trimethylsuccinic acid, which melted at 139—140°, and was in all respects identical with Bischoff's synthetical trimethylsuccinic acid. In the same year, Helle (*Inaug. Diss.*, Bonn, 1893), by the dry distillation of camphoronic acid, obtained a trimethylsuccinic acid melting at 131°, which, with acetyl chloride, yielded an anhydride melting at 31°; this acid he also considered was identical with the trimethylsuccinic acid prepared synthetically by Bischoff.

Early last year, the authors were desirous of preparing trimethylsuccinic acid in considerable quantity, and on studying the literature of the subject with the view of finding the best method of preparation, they found such a confused mass of experimental data, that it was very difficult to form any opinion in the matter, as the following acids had all been described as "trimethylsuccinic acid."

	Melting point.	K.	Authority.
(1.)	140—141°	0·0322	Zelinsky.
	139—140	0·0310	Bischoff, Koenigs.
(2.)	131	—	Helle.
(3.)	100—101	0·0063	Zelinsky.

Now, although Helle considered his acid to be identical with that prepared by Bischoff and Koenigs, the difference in the melting points tended to throw some doubt on his view, especially as he had obtained his acid so pure as to be able to subject it to a *detailed* crystallographic study. Even supposing the two acids were really identical, there still remained Zelinsky's acid of lower melting point to be accounted for. Trimethylsuccinic acid contains one asymmetric carbon atom, and therefore, according to the van't Hoff-Le Bel theory, it should only exist in *one* inactive form. If there are, as Zelinsky contends, *two* inactive modifications, then the theory in question is inadequate to explain the facts; the case being a crucial one, the authors decided to subject it to a careful re-investigation, some of the results of which are detailed in this paper.

Quite recently, February 1895, Auwers (*Ber.*, 28, 623) published a preliminary notice of some further work on the subject. On preparing trimethylsuccinic acid by every known method, he finds that it exists in *one* form only, melting at 147°, and yielding an anhydride which melts at 31°. He also brings further evidence against the view that Zelinsky's acid of lower melting point is a trimethylsuccinic acid, and finds that it is really a mixture of two $\alpha\alpha_1$-dimethylglutaric acids in molecular proportion, the one melting at 126° (*cis*), and the other at 140—141° (*trans*). The results of our experiments may be summarised as follows.

We have prepared trimethylsuccinic acid in quantity by two quite different methods, namely, the action of ethylic α-cyanopropionate on ethylic α-bromisobutyrate (Zelinsky's method), and by the action of ethylic α-bromisobutyrate on ethylic sodiomethylmalonate at 180° in xylene solution (Bischoff's method), and find that it undoubtedly only exists in *one* form, which melts at 152° (Auwers gives 147—148°), and yields an anhydride melting at 38·5° (Auwers gives 31°). Thus we are able to confirm Auwers' views as to the nature of this acid; with regard to the isomeric $\alpha\alpha_1$-dimethylglutaric acids, the authors have isolated two, one melting at 128° (cis-), and the other at 105° to 107°. Both these acids, on heating with acetic anhydride, yield the *same* anhydride, melting at 93° to 94°, which, with water, yields the cis-acid, melting at 128° again. The authors are engaged in an examination of the 105° acid, which is not yet complete enough for publication; up to the present, however, their results are not in agreement with those of Auwers.

During the course of their experiments, the authors have isolated ethylic αβ-dicyanopropionate, $CH_2(CN)\cdot CH(CN)\cdot COOEt$, a substance which crystallises in needles melting at 118°, and also trimethylcyanopropionic acid, $CH_3\cdot CH(CN)\cdot C(CH_3)_2\cdot COOH$, an interesting acid which crystallises in colourless needles melting at 126°, and, on treatment with acetic anhydride, yields a beautifully crystalline acetyl derivative, $CH_3\cdot C(CO\cdot CH_3)(CN)\cdot C(CH_3)_2\cdot COOH$, melting at 67°. The authors are engaged in further work on these acids, the results of which they reserve for a future communication.

EXPERIMENTAL PART.

Preparation of Ethylic α-Cyanopropionate, $CH_3\cdot CH(CN)\cdot COOEt$.

The ethylic α-cyanopropionate required for this investigation was prepared by the action of potassium cyanide on an alcoholic solution of ethylic α-bromopropionate. This reaction was first employed by Zelinsky (*Ber.*, 1888, **21**, 3162), who allowed the substances in question to interact on a water bath at the ordinary pressure. The yield of ethylic α-cyanopropionate was very unsatisfactory, as the product of the action contained not only a considerable quantity of unchanged ethylic α-bromopropionate, but also a large amount of ethylic dimethylcyanosuccinate, the latter being formed by the condensation of some of the ethylic α-cyanopropionate with the unchanged ethylic α-bromopropionate, as follows.

$$CH_3\cdot CH(CN)\cdot COOEt + CH_3\cdot CHBr\cdot COOEt = COOEt\cdot C(CH_3)(CN)\cdot CH(CH_3)\cdot COOEt + HBr.$$

Thus, from 258 grams of ethylic α-bromopropionate, he obtained 45 grams of unchanged substance, only 27 grams of ethylic α-cyanopropionate, and no less than 64 grams of ethylic dimethylcyanosuccinate.

The authors set to work to see whether by modifying the conditions of the experiment they could not improve the yield of ethylic α-cyanopropionate, and ultimately found that by working under pressure a much better result could be obtained. The method they finally adopted is as follows.

Fifty grams of finely-powdered potassium cyanide are added to a mixture of 100 grams of ethylic α-bromopropionate and 50 grams of absolute alcohol contained in a dry soda-water bottle; the bottle is then tightly corked and heated for six to eight hours at 100° in a water bath. It is found convenient to heat five or six such bottles at one time. The contents of the bottles, which are yellowish-brown (and in some cases dark brown), and smell strongly of hydrogen cyanide, are now filtered at the pump, and the residual potassium cyanide and bromide washed with a little alcohol. As much of the alcohol as possible is distilled off from the filtrate on the water bath, and the residue poured into water, when a reddish-brown oil separates; this is extracted with ether, the ethereal solution, after being well washed with water and dilute sodium carbonate solution, is dried over calcium chloride, and the ether distilled off. The residual reddish oil consists principally of three substances, namely, ethylic α-bromopropionate, ethylic α-cyanopropionate, and ethylic dimethylcyanosuccinate; these may be separated by careful fractionation, which is best effected under reduced pressure, using a fractionating column and a water condenser. Under a pressure of 30—40 mm., the unchanged ethylic α-bromopropionate distils for the most part between 77° and 85°, and then, if the fractionation has been carefully conducted, the thermometer rises somewhat rapidly to 103°, between which temperature and 110° ethylic α-cyanopropionate passes over as a colourless oil. It is well to interrupt the process at this juncture, and to continue the fractionation in an ordinary distilling flask without a column. The thermometer now rises very rapidly, and at a temperature of 195—200°, under 80 mm., ethylic dimethylcyanosuccinate passes over as a pale yellow oil; if this be very rapidly cooled, a small quantity of a beautifully crystalline solid separates out on the sides of the condenser, the investigation of which is described in the succeeding paragraph. The following table gives the quantities of the three principal products obtained by the modified process (from 100 grams of ethylic α-bromopropionate used) as compared with those got on employing the earlier method of Zelinsky.

	New.	Old.
Unchanged ethylic α-bromopropionate.......	28	33
Ethylic α-cyanopropionate..................	20	12
Ethylic αα-dimethylcyanosuccinate..........	10	7

Ethylic Dicyanopropionate, $CH_2(CN)\cdot CH(CN)\cdot COOEt$.

This substance is only formed in very small quantities in the foregoing experiment, the products of eight or ten bottles yielding only some 2 or 3 grams; it is deposited on the sides of the condenser in light, white flakes, during the distillation of the ethylic dimethylcyanosuccinate. It seems to be rather soluble in ethylic dimethylcyanosuccinate, and the more rapidly the vapour of the latter is condensed, the more of this solid body is obtained; it is fairly soluble in benzene, and, although almost insoluble in cold light petroleum, it may be crystallised from the hot solvent in beautiful, silky, pale yellow needles, which melt at 118°. On analysis, it yielded numbers closely agreeing with the empirical formula $C_7H_8O_2N_2$.

	Carbon.	Hydrogen.	Nitrogen.
Found	55·00	5·99	18·45 per cent.
Calculated ...	55·26	5·26	18·42 „

A determination of the molecular weight by Raoult's method gave the following results.

0·123 gram substance dissolved in 19·00 grams of benzene produced a depression of 0·215° in the freezing point.

$\therefore$ Molecular weight = 147·5. $C_7H_8O_2N_2 = 152$.

We concluded that the substance was ethylic $\alpha\beta$-dicyanopropionate, $CH_2(CN)\cdot CH(CN)\cdot COOC_2\cdot H_5$, and in confirmation of this view we found that, when boiled with concentrated hydrochloric acid for some time, it yielded ammonium chloride and an acid which gave the qualitative reactions of succinic acid, which should be formed according to the equation

$$CH_2(CN)\cdot CH(CN)\cdot COOC_2H_5 + 5H_2O = COOH\cdot CH_2\cdot CH_2\cdot COOH + C_2H_5\cdot OH + CO_2 + 2NH_3.$$

The formation of this substance probably takes place as follows. During the bromination of the propionic acid, a small quantity of the bromopropionic acid loses hydrogen bromide with formation of acrylic acid, according to the equation $CH_3\cdot CHBr\cdot COOH = HBr + CH_2{:}CH\cdot COOH$. This then combines with the excess of bromine to form $\alpha\beta$-dibrompropionic acid, $CH_2Br\cdot CHBr\cdot COOH$, the ethereal salt of which, when heated with potassium cyanide, yields the corresponding dicyano-compound. Other cases, somewhat similar to this, have been noticed in these laboratories.

Preparation of Ethylic Trimethylcyanosuccinate, $COOEt\cdot C(CH_3)_2\cdot C(CH_3)(CN)\cdot COOEt$.

The method employed for the preparation of this substance was essentially that proposed by Zelinsky (*Ber.*, 1891, **24**, 468), and may be briefly described as follows.

127 grams of ethylic α-cyanopropionate are mixed with a cold solution of 23 grams of sodium in 280 grams of absolute alcohol, and 205 grams of ethylic α-bromisobutyrate carefully added. There appears to be little or no action in the cold, but, on heating the mixture on the water bath in a reflux apparatus, sodium bromide soon separates, and, after some two hours, the solution becomes quite neutral. The contents of the flask are then poured into a large volume of water, when the ethylic trimethylcyanosuccinate separates as a dark yellow oil, which is extracted with ether. The ethereal solution is washed with water and dilute sodium carbonate solution, and dried over calcium chloride; the ether is then distilled off and the residual oil carefully fractionated under diminished pressure, when ethylic trimethylcyanosuccinate is obtained, boiling at 193—195° under a pressure of 40 mm. The yield is nearly theoretical.

Hydrolysis of the Ethereal Salt.

Zelinsky (*loc. cit.*) hydrolysed this ethereal salt by boiling it with dilute sulphuric acid; the authors, however, found this method very unsuitable, as, after heating for several days, a considerable amount of oil still remained unchanged. They decided therefore to employ alcoholic potash as the hydrolysing agent, and conducted the operation as follows.

The ethereal salt is slowly added to double its weight of potassium hydroxide dissolved in alcohol, and contained in a large flask; the addition is accompanied by a very considerable development of heat, and the flask, therefore, must be well cooled to prevent loss by frothing. A potassium salt separates almost immediately, and the contents of the flask become quite pasty, necessitating the addition of more alcohol. After all the ethereal salt has been added, the flask is connected with a reflux condenser and heated for 8—10 hours in a water bath, when a large amount of ammonia is evolved. The contents of the flask are then diluted with water until the potassium salt all dissolves, the solution poured into a large evaporating basin, and boiled vigorously for two or three days, fresh water and potassium hydroxide being added at intervals. To *completely* hydrolyse the ether is a matter of considerable difficulty, and we shall show that, after *continued* heating with potassium hydroxide in the manner just described until the evolution of ammonia nearly ceases, a very fair quantity of the potassium salt of trimethylcyanopropionic acid is left undecomposed. The alkaline liquid is concentrated to a small volume on the water bath, cooled, and carefully acidified with hydrochloric acid; it is then repeatedly extracted with pure ether, the ethereal solution dried over calcium chloride, the ether distilled off, and the residual oil heated in an oil bath at 200° until the evolution of carbonic anhydride entirely ceases.

In order to obtain the acids as pure as possible, it is advisable to distil the crude product under reduced pressure. Under a pressure of 100 mm. the greater part passes over between 190° and 260° as a colourless, pungent oil, consisting of a mixture of the acids and their anhydrides.

Separation of the Acids.—The anhydrides are converted into acids by dissolving them in hot water and evaporating the solution to dryness on the water bath; on cooling, a solid mass, consisting of the mixed acids, is left behind, which melts gradually between 70° and 95°. Zelinsky endeavoured to effect their separation by fractional crystallisation from a mixture of benzene and light petroleum, as stated in the introduction to this paper. The authors tried this method, but found that, although it was possible to effect a partial separation in this way, none of the fractions had a very definite melting point; fractional crystallisation from concentrated hydrochloric acid was then tried, but this gave still less satisfactory results. Finally, however, experiments on the fractional crystallisation of the calcium salts enabled the authors to devise a good method for isolating the pure acids, which is as follows. The mixture of the acids is dissolved in a small quantity of water, dilute ammonia added in slight excess, and, after heating the ammoniacal solution on the water bath for a short time, allowing it to remain overnight; a large crop of long, colourless needles of cyanotrimethylpropionic acid (A) separates, and are removed by filtration. On adding a little more ammonia to the filtrate and again concentrating, more of the needles are deposited on cooling; this operation is repeated until no more needles appear, even after the liquid has stood several hours. The clear liquid is now diluted in a large beaker with a considerable quantity of water, and mixed with an excess of calcium chloride solution. The beaker is now placed on a sand bath and its contents boiled for about half an hour, during which time the insoluble calcium salt (B) of trimethylsuccinic acid gradually separates. The liquid is now filtered while still hot, with the aid of the pump, and the calcium salt remaining behind is rapidly washed with a little hot water. If the filtrate is concentrated somewhat on the water bath, a further quantity of the calcium salt separates.

The mixed acids present in the filtrate as calcium salts are recovered by decomposing them with excess of strong hydrochloric acid, extracting with ether, and evaporating. The hard, crystalline residue, which melts gradually between 90° and 115°, is dissolved in a slight excess of dilute ammonia, and the whole process detailed above is repeated, when more cyanotrimethylpropionic acid and a further quantity of the insoluble calcium salt of trimethylsuccinic acid are obtained. Finally, the filtrate is again concentrated to a small volume on the water bath, decomposed by boiling with concentrated hydrochloric acid, and allowed to stand for some time, when a large crop of perfectly white crystals separates; these are collected, and, after recrystallisation from concentrated hydrochloric acid and drying on a porous plate, melt sharply at 127°. This substance (C) proved to be one of the modifications of $\alpha\alpha_1$-dimethylglutaric acid, which is much more insoluble in strong hydrochloric acid than the other isomeride.

The hydrochloric acid filtrate from this acid is again extracted with pure ether, the ethereal solution dried over calcium chloride, and the ether distilled off, when a solid acid is left, which melts gradually between 95° and 110°. On dissolving this in hot benzene, and allowing the solution to slowly evaporate at the temperature of the room, crystals are gradually deposited; when about half the benzene has volatilised, the liquid is poured off, and the acid is recrystallised from a small quantity of hot benzene, and dried on a porous plate. The crystals then melt at 105° to 107°.

As the benzene mother liquors still contain a considerable quantity of acid, the benzene is distilled off, and the oily residue is left for a week or two, when it becomes semi-solid; by careful treatment with benzene more of the acid, melting at 105° to 107°, may be obtained, but after as much as possible of this has been recovered an oil remains which is excessively soluble in benzene and water, and does not solidify even on standing in a vacuum several weeks at a low temperature (below the freezing point of water). This oil has not yet been investigated.

In this way, we have isolated from the original mixture of acids the four following compounds.

A. The colourless needles.
B. An insoluble calcium salt.
C. An acid melting at 127°.
D. „ „ 105° to 107°.

We shall now discuss these in detail.

A. *Trimethylcyanopropionic acid*, $COOH\cdot C(CH_3)_2\cdot CH(CH_3)\cdot CN$.

The colourless needles melted at 123—125°, but, after recrystallisation from hot concentrated hydrochloric acid, they melted sharply at 126°. They are sparingly soluble in cold water and in hydrochloric acid, but dissolve easily in these solvents on boiling, and separate again on cooling. The acid is fairly soluble in cold benzene, but insoluble in cold light petroleum, or in a mixture of benzene and light petroleum; it is very readily soluble in chloroform or alcohol.

On analysis the following numbers were obtained, which agree well with the empirical formula $C_7H_{11}O_2N$.

	Carbon.	Hydrogen.	Nitrogen.
Found	60 01	7·88	10·23, 9·88 per cent.
Calculated...	59 58	7·80	9·99 ,,

This acid is an interesting substance in many respects. If a solution of its ammonium salt is heated on a water bath, the salt decomposes, ammonia is evolved, and, on cooling, the free acid separates. Although the acid contains a cyanogen group, it may be recrystallised from hot concentrated hydrochloric acid without decomposition; in fact, it is only on *prolonged* heating with the ordinary hydrolysing agents that it is decomposed.

The silver salt was prepared by dissolving the acid in dilute ammonia, gently warming the solution to get rid of the slight excess of ammonia present, and then adding rather more than the calculated quantity of silver nitrate dissolved in water. No precipitate was formed, but, on slowly concentrating the solution in a dark room at a moderately low temperature, colourless needles separated. These were collected with aid of the pump, quickly washed with cold distilled water, in which they are rather soluble, and dried in a vacuum over sulphuric acid. The salt must be kept in a dark place, as it is rather readily acted on by light.

On analysis the following numbers, corresponding with the formula $C_7H_{10}O_2NAg$, were obtained.

	Silver.	Carbon.	Hydrogen
Found	43·90, 43·86	33 20	4 11 per cent.
Calculated...	43·55	33·89	4 03 ,,

Acetyl Derivative, $COOH\cdot C(CH_3)_2\cdot C(CH_3)(CN)\cdot COCH_3$.—A small quantity of the acid was heated for 10 hours with excess of acetic anhydride in a small reflux apparatus on a sand bath. After the excess of acetic anhydride had been distilled off under a pressure of 200 mm., the receiver was changed, when a colourless oil distilled over at a temperature of 240°; this, on cooling, solidified to a crystalline mass melting at 60—63°. It is very soluble in acetic anhydride, but it may be obtained in beautiful colourless crystals by allowing an acetic anhydride solution slowly to concentrate in a vacuum over solid potash. It may be recrystallised from hot light petroleum, and, when pure, melts sharply at 67°.

On analysis, it gave the following numbers

	Carbon.	Hydrogen.	Nitrogen.
Found	58·7	7·29	7·89 per cent.
Calculated ($C_9H_{13}O_3N$) ...	59·01	7·10	7·65 „

On warming the acetyl derivative for a few minutes with concentrated hydrochloric acid, it dissolves, and, on cooling, the solution deposits long needles of the original acid, melting at 126°.

The Constitution of the Acid.—This was determined by boiling it for several hours in a reflux apparatus with concentrated hydrochloric acid; on cooling, white crystals of trimethylsuccinic acid were deposited, which, after recrystallisation, melted at 150° (see B). The filtrate was found to contain ammonium chloride. These reactions show that the acid has the constitutional formula

$$COOH{\cdot}C(CH_3)_2{\cdot}CH(CH_3){\cdot}CN.$$

B. *The Insoluble Calcium Salt of Trimethylsuccinic acid,* $COOH{\cdot}C(CH_3)_2{\cdot}CH(CH_3){\cdot}COOH$.

This calcium salt (B) was decomposed by dissolving it in hot, strong hydrochloric acid; on allowing the solution to cool, a mass of hard greyish-white crystals separated, which, when collected and dried on a porous plate, melted at 138 to 142°, but on recrystallisation from concentrated hydrochloric acid the melting point was raised to 145° to 149°. To further purify the acid, it was dissolved in hot water, a slight excess of dilute ammonia added, and the acid again precipitated as calcium salt by boiling with excess of calcium chloride. The calcium salt was collected, washed well with water, and the acid again regenerated by boiling with concentrated hydrochloric acid. The filtered solution, on standing, deposited perfectly white, hard crystals, which, after being dried first on a porous plate and then at 100°, melted sharply at 151—152°. On analysis the acid gave the following numbers:—

	Found.	Calculated for $C_7H_{12}O_4$.
Carbon	52·47	52·50 per cent.
Hydrogen	7·23	7·50 „

Trimethylsuccinic acid is fairly soluble in cold water, but almost insoluble in cold concentrated hydrochloric acid. In warm benzene it is very readily soluble, but only sparingly in hot, and quite insoluble in cold light petroleum. It readily dissolves in alcohol and chloroform.

Dr. Walker has kindly determined the dissociation constant of this acid for us. He obtained the value K = 0·0302, which agrees closely with the number K = 0·0304 given by Auwers (*Ber.*, 1895, **28**, 265).

Anhydride of Trimethylsuccinic acid.—In order to prepare this, 4 grams of the acid were heated on a sand bath for six hours with excess of acetic anhydride in a small flask, into which a condensing tube was ground. The contents of the flask were then transferred to a small distilling flask, and after the excess of acetic anhydride had been distilled off under a pressure of 200 mm., the receiver was changed and the residual oil distilled over. As the colourless distillate still contained a small quantity of acetic anhydride, it was allowed to stand on a watch-glass in a vacuum over solid potash for two or three days; beautiful colourless crystals gradually formed, which, after drying on a porous plate in a vacuum, melted sharply at 38·5°. On analysis, the following numbers were obtained corresponding with those required for the anhydride of trimethylsuccinic acid.

	Found.	Calculated for $C_7H_{10}O_3$.
Carbon	58·79	59·15 per cent.
Hydrogen......	6·95	7·00 „

On dissolving a portion of the anhydride in a little hot hydrochloric acid, and allowing the solution to cool, it deposited white crystals of the original trimethylsuccinic acid melting at 150°.

We may here remark that in his recent paper (*Ber.*, 1895, 28, 263), Auwers describes this anhydride as melting at 31°, which is also the same melting point as that observed by Helle (*Inaug. Diss.*, Bonn, 1893). Neither of these investigators appear to have obtained it quite pure.

The results we have thus recorded show that the acid from the insoluble calcium salt is probably identical with the trimethylsuccinic acid described by Zelinsky as melting at 140—141°. It must also be the same as the acid described by Helle as melting at 131° and yielding a very insoluble calcium salt and an anhydride melting at 31°; and, lastly, the same as the acid recently described by Auwers as melting at 147—148°, and giving an anhydride melting at 31°.

C. cis-*Dimethylglutaric acid*,

$COOH \cdot CH(CH_3) \cdot CH_2 \cdot CH(CH_3) \cdot COOH$.

We were at first inclined to think that this acid was the same substance as the needles melting at nearly the same temperature (see (A)). However, on mixing as nearly as possible equal quantities of the two, and making a melting-point determination, we found that the mixture began to melt at 90°, and continued to do so until the thermometer rose to 105°; this showed that the two acids were different; we subsequently found that they yielded different compounds when treated with acetic anhydride, and, finally, that whereas the needles contained nitrogen, the other substance did not. The acid appeared to have the same properties as the dimethylglutaric acid described by Zelinsky (*Ber.*, 1889, **22**, 2823) as melting at 128°, and the following analytical results bore out that conclusion.

	Found.	Calculated for $C_7H_{12}O_4$.
Carbon	52·73	52·50 per cent.
Hydrogen......	7·55	7·55 „

It is moderately soluble in water, but almost insoluble in cold concentrated hydrochloric acid. In benzene it is rather soluble, but not so readily as the acid D; it is insoluble in light petroleum, but readily soluble in alcohol and chloroform.

Anhydride of cis-*Dimethylglutaric acid.*—A small quantity of the acid was heated with excess of acetic anhydride on a sand bath for three hours in a small reflux apparatus; the contents of the flask were then transferred to a small distilling flask, and the excess of acetic anhydride distilled off under reduced pressure (100 mm.). The receiver having then been changed, the pressure was further reduced to 40 mm., and the distillation continued, when the anhydride of cis-dimethylglutaric acid passed over at 180° to 185° as a colourless oil, which solidified on cooling. It was recrystallised from acetic anhydride, and the crystals dried on a porous plate in a vacuum over solid potash. It melted sharply at 93·5°. On redissolving it in hot hydrochloric acid and allowing the solution to cool, crystals of the original acid were deposited, which, on drying, melted at 128·5°. This indicates that the dimethylglutaric acid melting at 128° is the *cis*- modification.

Dr. Walker kindly determined the dissociation constant of this acid and found K = 0·0056.

D. *The Acid melting at* 105° *to* 107°.

This acid is doubtless identical with the compound Zelinsky obtained by the same reaction as ourselves, and which he found melted at 100° to 101°, and had a dissociation constant K = 0·0063 (*Ber.*, 1891, **24**, 459). He, however, still maintains that it is a trimethylsuccinic acid, whereas we shall show that it must be a dimethylglutaric acid. We may here remark that it is exceedingly difficult to get this substance quite free from the higher melting cis-dimethylglutaric acid, and it does not usually melt quite sharply, but this is a point to which we shall have occasion to refer again. The acid is readily soluble in benzene, but much less so if a little light petroleum be added to the solution; in light petroleum itself, it is almost insoluble. It is very soluble in water, but only sparingly in concentrated hydrochloric acid, it is, however, rather more soluble in this last named liquid than cis-dimethylglutaric acid.

The acid on analysis gave the following numbers :—

	Found.	Calculated for $C_7H_{12}O_4$.
Carbon........	52·10	52·50 per cent.
Hydrogen......	7·34	7·50 „

The dissociation constant of this acid determined by Dr. Walker is K = 0·0057.

Conversion into the Anhydride.—The acid was heated with excess of acetic anhydride in a reflux apparatus for four hours on a sand bath. The acetic anhydride was first removed by distillation under reduced pressure, and then the anhydride of dimethylglutaric acid passed over; it is a colourless oil, which solidified to a white mass on cooling, and, after recrystallisation from acetic anhydride, and drying on a porous plate in a vacuum over potash melted at 93—94°.

The crystals, on analysis, gave the following numbers.

	Found.	Calculated for $C_7H_{10}O_3$.
Carbon........	59·13	59·15 per cent.
Hydrogen......	6·98	7·00 „

The anhydride was converted into the acid by dissolving it in hot concentrated hydrochloric acid, the solution on standing depositing white crystals melting at 128·5°.

Thus it will be seen that the two acids described under C and D, melting at 128·5° and 105—107° respectively, yield the *same* anhydride, melting at 93—94°, which with water yields the acid of higher melting point. There can therefore be no doubt but that Zelinsky is wrong in calling the acid (m. p. 100—101°) which he obtained a trimethylsuccinic acid.

As stated in the introduction to this paper, Auwers has recently published experiments calling in question the homogeneous character of this acid (*Ber.*, 1895, **28**, 269). He regards it as a mixture in molecular proportion of the acid we have described as cis-dimethylglutaric acid, melting at 127°, and a new dimethylglutaric acid (trans-), melting at 140° to 141°. He separated these acids, either by means of their calcium salts or by treatment with acetyl chloride; in the latter case the cis- acid present is readily converted into the anhydride in the cold, whereas the trans- acid is unchanged, acetyl chloride converting it into the anhydride only after continued heating of the mixture in a sealed tube. Up to the appearance of Auwers' last paper, the authors never found anything which threw doubt upon the homogeneous nature of their 105° acid. It is true that it did not melt quite sharply, but this they always thought was due to the presence of a very small amount of the cis- acid, the last traces of which are very difficult to remove. The authors have done much work on this acid, which so far has yielded some very remarkable results, differing very materially from those recently published by Auwers; probably when the latter publishes a more detailed account of his work the discrepancies between their results and his will be explained, but they are subjecting this acid to a thorough examination, and must reserve the results for a future communication.

Preparation of Trimethylsuccinic acid by Bischoff's Reaction.

Bischoff and Mintz (*Ber.*, 1890, **23**, 647), by the action of ethylic α-bromisobutyrate on the sodium compound of ethylic methylmalonate in alcoholic solution at 100°, and subsequent hydrolysis of the ethereal salt produced, obtained as principal product an acid melting at 105°; this they at first described as trimethylsuccinic acid, but afterwards came to the conclusion that it was a dimethylglutaric acid. A little later Bischoff (*Ber.*, 1891, **24**, 1041) found that by conducting the reaction in xylene solution at 180° he obtained, besides this dimethylglutaric acid, a trimethylsuccinic acid melting at 139·5°. Helle (*Inaug. Diss.*, Bonn, 1893), on repeating this synthesis, obtained an acid melting at 131°, and yielding an anhydride melting at 31°. He also found the same acid was formed by the dry distillation of camphoronic acid. The question at once arises are these acids, prepared by Bischoff and Helle, identical with the trimethylsuccinic we have described already, and if not, are they trimethylsuccinic acids at all? To decide this point, we repeated their work, and found that one of the acids formed melted at 151°, and was in all respects identical with the trimethylsuccinic acid we prepared by Zelinsky's method.

Interaction of Ethylic α-Bromisobutyrate and Ethylic Sodiomethylmalonate in Xylene Solution at 180°.—One hundred and three grams of ethylic methylmalonate were dissolved in 150 c.c. of xylene contained in a round-bottomed flask, and 13·3 grams of sodium in the form of wire added in two portions. The sodium gradually dissolved in the cold, but much more rapidly if the flask was gently warmed on a sand bath, and at the same time the sodium compound of ethylic methylmalonate separated as a brownish, pasty mass. As soon as the sodium had completely disappeared, the flask was cooled, 106 grams of ethylic α-bromisobutyrate were carefully added, and the whole boiled in a reflux apparatus in an oil bath for two days. As soon as the mixture had acquired a neutral reaction, it was poured into water, and the oily layer which separated mixed with ether; the ethereal solution, washed first with dilute sodium carbonate solution and then with water, was dried over calcium chloride, and the ether distilled off. The residue was now distilled under a pressure of 45 mm., when, between 90° and 100°, a large quantity of xylene came over, and then between 140° and 155°, some 20 grams of oil, mostly unchanged ethylic methylmalonate. The receiver was now changed, and the fractionation continued; the temperature rose somewhat rapidly to 170°, and from this point very slowly to 200°, most of the oil, however, seemed to distil over at two temperatures, namely, 185° and between 195° and 200°. The fraction passing over between 170° and 200° amounted to about 55 grams, and about 20 grams of a residue of higher boiling point was left in the retort.

Hydrolysis of the Oil boiling between 140° *and* 200°.—The two fractions obtained above, boiling at 140—155° and 155—200° respectively, were united and added to 90 grams of potassium hydroxide dissolved in alcohol. The mixture was then heated in a reflux apparatus for six hours on a water bath, during which time a quantity of potassium salts separated. The contents of the flask were then poured into water, and after the solution had been evaporated in a large basin on the water bath until all the alcohol had volatilised, the liquid was acidified with hydrochloric acid, and the acids extracted by repeatedly shaking with pure ether. The ethereal solution was dried over calcium chloride, the ether distilled off, and the residual oil heated at 200° until all evolution of carbonic acid had ceased. On distilling the thick oily residue under a pressure of 30 mm., a considerable portion, *A*, passed over between 130° and 200°, the thermometer rising steadily all the time; this contained a good deal of propionic acid. The receiver was changed at 200°, and the oil, *B*, passing over between 200° and 250°, was collected; these two fractions were then worked up separately.

Fraction A (130—200°).—This smelt strongly of propionic acid, but on adding dilute ammonia in excess a large amount of oil remained undissolved in the cold, although on boiling everything went into solution. The liquid was then diluted and boiled with animal charcoal, filtered, and to the filtrate, which was pale yellow, a solution of 30 grams of calcium chloride was added. On boiling the liquid on a sand bath, a large quantity of an insoluble calcium salt separated, which was collected with the aid of the pump. The filtrate contained the more soluble calcium salt of an acid melting at 104—107°.

Fraction B (200—250°).—This was treated in exactly the same way as A, but only a very small quantity of the insoluble calcium salt was obtained, this fraction largely consisting of the acid of lower melting point.

Decomposition of the Insoluble Calcium Salt.—The calcium salt, dissolved in excess of hot and strong hydrochloric acid, yielded colourless crystals on cooling, which, after being separated from the mother liquor and dried, melted at 140—148°. The acid was purified by redissolving it in ammonia, reprecipitating as calcium salt, and decomposing this with hot hydrochloric acid, &c. In this way the acid was obtained as a colourless, crystalline powder, melting at 150°; on recrystallisation from hydrochloric acid its melting point rose to 151°.

The acid gave the following numbers on analysis.

	Found.	Calculated for $C_7H_{12}O_4$.
Carbon	52·41	52·50 per cent.
Hydrogen......	7·72	7·50 ,,

It was in every respect identical with the trimethylsuccinic acid prepared by Zelinsky's method, melting at 152°.

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XLVII.—*Contributions to the Chemistry of Cellulose.*

By C. F. Cross, E. J. Bevan, and C. Beadle.

In a monograph recently published, we have undertaken the task of setting out, under a definite scheme of classification, the properties, and also the reactions of synthesis and decomposition of the celluloses and compound celluloses. The work of the last 15 years, in which many have been engaged, has resulted in a formidable accumulation of experimental matter. The numerous contributions to the subject are necessarily wanting in cohesion to those who follow it with only a general interest, for the obvious reason that cellulose is not investigated under the leading of a dominant theory; in this respect, it presents a marked contrast to the group of simpler carbohydrates, to which, on the other hand, it has a fundamental and long-recognised relationship. The constitutional problems presented by this group have been elucidated by recent classical investigations, and their solution carries with it an important advance of the general theory. The chemistry of cellulose lacking these features of attractiveness has therefore but a limited claim on the attention of students of theory, although it has other claims which are fully admitted, and in its later developments may be expected to contribute to the general advance of the science. From these points of view, present and prospective, it was thought opportune to attempt a systematic *résumé* of the subject matter, first, to give it the coherence which naturally follows from a systematic classification based upon well-established lines, and secondly, to clear the way for the elucidation of the special constitutional problems connected with it.

We may, perhaps, be allowed a personal "apology" in reference to this work. We are aware that in many of our publications on this subject, we have been found wanting in method and lucidity. With no desire to elude the force of these criticisms, we plead that we have never felt justified in overloading special communications with such details as are, perhaps, required for the complete elucidation of the problems involved but may more properly be given in an independent publication. We still are of opinion that particular contributions to this subject must assume a knowledge of previous publications: and in what follows we proceed upon the basis formulated in our recently published monograph.

The problem of the constitution of the typical *cellulose is being opened out in certain definite directions which may be briefly noted.

I. *Hydrolysis.*—In resistance to hydrolysis, cellulose stands in marked contrast to starch. The difference in their behaviour on treatment with dilute acids and alkalis need not be enlarged upon. The thiocarbonate reaction of cellulose, with its preliminary conversion into alkali cellulose, followed by treatment with carbon bisulphide, dissolution, and the varied treatment to which it is subjected for the regeneration of the cellulose, is unattended by conversion into soluble products. The yields of regenerated cellulose are quantitative, and the composition of the product indicates only fractional hydration, that is, from $C_6H_{10}O_5$ to $4C_6H_{10}O_5,H_2O$. With starch, we have been unable to effect this reaction; and although there are certain points of resemblance to cellulose in its behaviour with alkalis, the product (alkali starch) differs from alkali cellulose in this important particular; moreover, the starch molecule is considerably broken down (hydrolysed) by prolonged contact with alkali and water.

In regard to acid hydrolysis, the recent systematic study by A. L. Stern (this vol., 74) of the interaction of cellulose and concentrated sulphuric acid emphasises an important point. The conversion into the disulphuric ester formed as the first product of the action is not attended with liberation of CO-groups. Further, the subsequent hydrolysis of the product by boiling (with 2—3 per cent. H_2SO_4) may be pushed to a very considerable length without any hydrolysis of this character taking place. Therefore, although cellulose is ultimately hydrolysed to dextrose by this process, the intermediate stages of the dissection show that the cellulose structure is very different from that of starch. Cellulose, in fact, is not a polyaldose or aldosan of the starch type, and its structure cannot be explained by simple carbonyl linking.

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* By the "typical cellulose" is to be understood the substance of a normal bleached cotton, and the same applies to the term "cellulose" wherever employed, in this paper, without qualification.

We have long been impressed with this distinction of configuration, and therefore have by preference followed up those synthetical reactions which are best calculated to bring out the distinctive behaviour of cellulose. These have disclosed a well marked differentiation in function of its OH-groups, the result being a further widening in the constitutional gap between cellulose and starch. As bearing on this point, we may instance the results of the further study of

II. *The Esters of Cellulose.*—It is obvious that a complete investigation of cellulose in regard to the number and functions of its OH-groups must solve in general terms the constitutional problem. For a long time, the view prevailed that the unit formula should be written $C_6H_7O_2(OH)_3$, the highest known esters being the trinitrate and triacetate. In regard to the nitrates, it was obvious that they were formed without the molecular weight of the parent complex being affected; this conclusion might fairly be drawn, for example, from the external features of the original fibre remaining unchanged. The recent achievements in the spinning of these nitrates in continuous threads, followed by the process of denitration of these threads, without affecting their physical properties (lustre and continuity or tensile strength), furnish conclusive evidence of the persistence of the cellulose configuration. But the evidence to be drawn from these alcoholic nitrates is not conclusive as to the maximum number of OH-groups in the original molecule.

We therefore made a further investigation of the acetates, and succeeded in obtaining—by Franchimont's method of acetylation—products having the composition of tetracetates, and, in some cases, of pentacetates of the unit group, $C_6H_{10}O_5$. The formation of the former could be interpreted as a simple process of acetylation of the group $n[C_6H_6O(OH)_4]$, but, in the case of the pentacetate, the cellulose complex must undergo hydrolysis. We attempted to solve the point by molecular weight determinations of the acetates by Raoult's method, but the results were anomalous, and no conclusions could be drawn from them, save that these esters, when dissolved in acetic acid, appeared to undergo dissociation into unit groups of much smaller dimensions.

The investigation was reopened with the observation that the cellulose regenerated from the thiocarbonate reacted directly with acetic anhydride at its boiling point; under these conditions as there was no hydrolytic agent present, such as zinc chloride, the acetylation may be assumed to be of a simple character. The acetates thus prepared were repeatedly analysed, and the numbers obtained again showed the formation of a tetracetate, $C_6H_6O(OAc)_4$.

As this method of acetylation was somewhat tedious, requiring prolonged digestion with the anhydride, we took advantage of the greater activity of the cellulose in this form, and devised a method of acetylation which could be carried out at low temperatures; this throws further light not only on this particular process, but generally on the functions of the OH-groups in cellulose. The regenerated cellulose (hydrate), after washing, is mixed with an equivalent of zinc acetate in concentrated aqueous solution, and the mixture dried first on a water bath, and finally at 105°. The cellulose, in presence of zinc acetate, reacts with acetyl chloride at 30°, and the higher acetates are directly formed. In the analysis of the products of this action, we were able to arrive at a definite criterion as between the tetracetate and acetates containing a still higher proportion of acetyl. The acetates were prepared for analysis in the state of films of $\frac{1}{100}$ to $\frac{1}{20}$ mm. in thickness. It was found, on saponification, that the products showed the following differences.

Higher Acetates.—The films were disintegrated by the alkali, and the products of hydrolysis reduced Fehling's solution.

Lower Acetates.—The cellulose obtained, on saponification, retained the form of a transparent continuous film, and the alkaline solutions were entirely without reducing action (on CuO). It appears, therefore, that cellulose can be acetylated up to the state of tetracetate without hydrolysis, at least such as gives rise to the liberation of CO-groups; in other words, the special configuration of cellulose is maintained when 4OH-groups are replaced by negative radicles.

If, therefore, the unit-group of cellulose is formulated as $C_6H_6O(OH)_4$, and the remaining oxygen atom is present as CO, it is impossible to represent the cellulose complex as a polyaldose. In the absence of further evidence we should be limited to speculative views as to the type of CO-condensation characteristic of the celluloses; our investigations, however, have broken ground in a new direction, and the results obtained may be briefly noticed for their bearing on the constitutional problem.

III. *Electrochemical Phenomena of Cellulose.*—In many of its reactions, cellulose presents the characteristics of a salt; for instance, the fact that it dissolves in zinc chloride solution admits of no other explanation than as being the result of a simultaneous and reciprocal interaction of the acid and basic groups of the two substances. The process of acetylation above described, namely, treating the cellulose with zinc acetate and exposing the mixture to the action of acetyl chloride, is only to be explained as the result of a species of double-salt combination between the cellulose and the zinc acetate. The whole range of dyeing phenomena critically illustrates this species of activity not only of the celluloses but also of the other organic colloïds such as silk, wool, gelatin, &c. In development of this view, we have recently investigated the behaviour of cellulose as an insulator *or* transmitter of the electric current. On comparing the various celluloses in the air-dried condition, we found that their insulating powers were approximately in inverse proportion to the percentages of hygroscopic moisture. On moistening the celluloses with water, the current was transmitted, and from the phenomena to be described, the conductivity appears to result from a definite but partial electrolysis of the cellulose molecules.

On moistening Swedish filter-paper and placing it between two metallic surfaces acting as terminals of a battery, the current is completed through the paper, the metal of the positive conductor is attacked, carried forward in the direction of the current, and deposited in the paper in combination with the cellulose. The phenomena are perhaps most characteristic in the case of silver, and to convey a more definite impression of what takes place we will describe an actual experiment. A small battery, giving a current of 1/50 Ampère with a difference of potential between the terminals of 4—6 volts, is connected with a silver plate (+) which may, for instance, carry a design in sharp lines in relief, whilst the negative is connected with a plate of any other metal—copper, for example. Swedish paper just moistened with water (retaining 40—50 per cent. of its weight) is laid on the copper, and the silver terminal (+) is laid upon it with slight pressure for a period of 1—3 seconds. With short contact, the silver is deposited as a silver compound, and on plunging the paper into a reducing solution the design is developed in deep black lines of metallic silver. With longer contact, the design is brown (silver oxide), and rapidly disappears on treatment with dilute acetic acid. On reversing the current, the contact being maintained, this brown stain is rapidly converted into the black of metallic silver as the result of secondary electrolysis.

A considerable range of these phenomena has been investigated, and will be described in the experimental portion of this paper. The results appear to be most simply interpreted as following from a partial breaking down of the cellulose aggregate in presence of water. Assuming that in the molecule the OH-groups in proximity to the CO-groups are negative in function, and the corresponding basicity of the remaining OH-groups is conditioned by proximity to a CH_2-group, it is not very surprising that the molecule should respond to the special influence of the electric current much in the same way as a salt. The attack on the positive terminal would be on this view a direct action of the negative OH-groups of the cellulose itself, and this, after considerable investigation, appears to be the most reasonable explanation. If this view be accepted, or rather proved beyond doubt, it may be applied in various directions to account for many other special reactions of the carbohydrates, for they all appear to share with cellulose this tendency to a species of electrolytic strain and decomposition. In the simpler carbohydrates, the tendency to migration of the oxygen and hydrogen within the molecule is seen in the numerous decompositions attended by rupture of the carbon nucleus, which are determined by hydrolytic agencies, such as fermentation, resolutions by dilute acids and alkalis, with production of acid bodies on the one hand, and on the other of compounds proportionately less rich in oxygen. This species of polarity is undoubtedly a general characteristic of the carbohydrates, and certainly persists in the complex aggregates of such molecules of which the celluloses are built up. In the latter, however, the property is modified by their special configuration, so that, unlike those lower in the series, they strongly resist disintegration; at the same time, however, they respond to electrolytic action in the way above described, and this property must be taken into account in a comprehensive view of the constitution of the celluloses in regard to their chemical activity, and especially in those reactions which underlie their functions in organised tissues.

This brief statement of such evidence as we have, leads us to the following conclusions as to the constitution of the typical cellulose :— (1) It is differentiated in the most marked way from starch; it has the characteristics of a homogeneous compound rather than an aggregate of aldose groups united by O-linking of the least resistant type. (2) Since it forms derivatives of the general formula $n[C_6H_6O(OH)_4]$ without loss of any of the essential characteristics of cellulose compounds, it is probable that the synthesis of the individual C_6-groups takes place by carbon and not by oxygen linking. This hypothesis is also consistent with the observation that the cellulose aggregate may be considerably resolved without liberation of CO-groups. (3) The reactions of cellulose cannot at present be generally expressed by any constitutional formula. It may be noted, however, as definitely established that of the four OH-groups in the C_6-unit two are basic and two acidic, as indicated by the following characteristic reactions.

(*a*) *With acid hydroxyls:* Formation of alkali-cellulose,

$$[C_6H_{10}O_5,2NaOH],$$

and subsequent reactions with carbon bisulphide (xanthate) and with benzoic chloride (dibenzoates). (*b*) *With basic hydroxyls:* Formation of disulphuric esters. The reactions of cellulose therefore in many directions are those characteristic of salts or ethers.

(4) The celluloses in presence of water, like other colloïds, show the property of conducting the electric current, sustaining an electrolytic strain, or partial electrolysis. In consequence of this strain, its OH-groups are brought into a state of reactivity.

The above discussion relates, as stated, to the typical (cotton) cellulose in the condition of bleached and purified fibre.

Progress has been made in the classification of the celluloses, and the cellulose group may now be divided as follows.

1. Celluloses resisting hydrolysis (chiefly fibrous celluloses).
2. Celluloses easily hydrolysed (chiefly cellular celluloses).

Group 1 is divisible into three sub-groups having the following characteristics:—Greater or less resistance to hydrolysis and oxidation, ratio of carbon to oxygen, and proportion of furfural which they yield on treatment with acids.

	* Cotton sub-group. A.	Wood cellulose sub-group. B.	Cereal cellulose sub-group. C.
Type	Cotton	Jute cellulose	Straw cellulose.
Percentage C	44·0—44·5	43·0—43·5	41—42
Percentage O	50·0	51·0	53·0
Furfural	0·1—0·4	3·0—5·0	12·0—15·0
Other characteristics	No active CO-groups. Quantitative regeneration from solution as xanthate.	Some free CO-groups. Partly hydrolysed by xanthate process	Considerable reactivity of CO-groups. Red reaction with aniline salts. Considerably hydrolysed by xanthate process.

Group 2 comprises celluloses of the starch type of aggregation easily hydrolysed to hexoses and pentoses, and termed Hemicelluloses (Schultze).

This classification is at this date sufficiently comprehensive and distinctive to embrace and differentiate the experimental material to hand. It also indicates as an immediate object of research the determination of the functions and mode of union of the O-atoms in the unit group of the cereal celluloses. These compounds are pronounced furfurose derivatives. They have a higher O : C ratio than the hexoses or their anhydro-derivatives, and their empirical composition is more nearly that of the pentoses or pentosans, which it has been stated they contain. They yield furfural, however, in much smaller

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* It will be understood, of course, that the celluloses here classified are considered as *isolated* by the standard processes of purification from the raw materials as they occur in the "*natural*" world.

proportion than the latter group, and the yield is largely reduced as a result of deoxidising treatment (*infra*). The alternative is the probable presence of CO·O-groups or of diketohexane derivatives. Expressing this alternative view in general terms, they are oxycelluloses, resulting either from oxidation of normal celluloses after their elaboration by the plant, or from the elaboration of oxidation products of the hexoses into cellulosic complexes. These considerations open out in definite terms a fundamental problem of plant physiology, that is, whether the reduction of CO_2 is terminated in all cases by the synthesis of hexoses, or whether, assuming that the plant always proceeds to the elaboration of its permanent tissue by way of aldoses, the tissue substance (cellulose) is afterwards oxidised as an incident of the general functions of the stem or leaf. This problem of elaboration in relation to the furfuroses or furfurosans of plant tissues could not be expressed in the above terms so long as it appeared probable that the pentoses were direct products of assimilation. The extended researches of De Chalmot (*Amer. Chem. Jour.*, 15, 16) have, however, negatived this view of their origin. They are products of metabolism, and no doubt derived from the hexoses as secondary products formed by a process of limited oxidation. A part of our investigation has been devoted to the further elucidation of this problem, and the evidence goes to show (1) that oxidised derivatives of the hexoses may be and are elaborated into permanent tissue (cellulose), and (2) that the tissue celluloses are further oxidised as an incident of their normal functions. It is clear, of course, that assimilation is accompanied by processes of severe oxidation, and it is more in accordance with modern views to regard these oxidised products—such as oxalic and tartaric acids—as formed by the destructive oxidation of products of assimilation rather than as intermediate and direct products of deoxidation of carbonic acid. The only objection to extending this view to the celluloses of plants is the *a priori* consideration of general economy, which would lead us perhaps to regard the fundamental tissue as permanent and protected from destructive oxidation. It should be remembered, however, that the conversion of the celluloses into oxycelluloses is not necessarily a process of destructive oxidation. Even in laboratory processes of oxidation, by chromic acid and by hypochlorites, for example, the celluloses preserve their essential characteristics, and the fixation of oxygen is not accompanied by fundamental molecular changes. It would not be difficult, further, to account for such oxidations of the permanent tissues of cereals. The universal distribution of nitrates in the growing tissues is in itself an index of the occurrence of oxidising processes in which they are directly concerned, apart from oxidations by active oxygen in its various forms. And to put the matter still more generally, it appears from the evidence accumulated that the three important directions of modification of cellulose in the plant, namely, lignification, suberisation, and "pectification" are all determined by oxidising actions. The products of the first two are characterised by the presence of furfuroïds, which, as already stated, must be regarded as derived from the hexoses, and the last contain the pectic compounds which are acid in character, and have a much higher $O : CH_2$ ratio than the carbohydrates. The constitution of these products, moreover, indicates a union of the products of oxidation with the alcoholic groups of unaltered cellulose; they are, in fact, cellulose esters, and the formation of such derivatives has an obvious physiological significance, modifying both the chemical and physical properties of the tissues in accordance with the specialisation of function and the varying requirements of the plant in relation to both internal and external influences.

In addition to these more general directions of investigation, special points have been worked at from an empirical point of view. Thus it was of interest to throw more light on the mechanism of the production of furfural from the pentoses and oxy-hexoses. In their characteristic decomposition volatile acids are formed, and we have made careful observations to determine (1) whether they are formed in any constant relation to the furfural, and (2) the composition of these acids produced from various fibrous products, under varying conditions. We find that these acids are generally mixtures of formic and acetic acids, the former predominating in most cases. In the cereal straws, on the other hand, acetic acid is the main product. These products are formed, under certain conditions, in constant relationship to the furfural, whilst in others they appear to result from an independent and parallel decomposition of the parent substance.

EXPERIMENTAL PORTION.

Cellulose in Relation to Hydrolysis and Hydration.

No reactions of cellulose hitherto studied have thrown so much light on the problems involved in the subject of this section, as those by which it can be converted into xanthate and reconverted into cellulose (Trans., 1893, **63**, 837). The experiments about to be described establish the following points.

I. Celluloses of the cotton group pass through the cycle of changes without undergoing hydrolysis to form soluble derivatives.

II. Celluloses of the other two groups (p. 439) are partially hydrolysed. The composition of the regenerated cellulose is different from that of the original cellulose, chiefly in respect of the proportion of furfural yielding groups; this in the case of the cereal celluloses being reduced by about five-sixths The yield of furfural in the remaining soluble portions is also so far reduced that the total reduction amounts in the aggregate to 50 per cent.

III. The compound celluloses are only partially resolved by the thiocarbonate reaction. The woods may be taken as resisting altogether: the lignocelluloses of annuals are attacked in a remarkable way, swelling up to an enormous extent with water, but dissolving only to the extent of 30—50 per cent. The pectocelluloses (flax, &c.) are largely converted into soluble derivatives (alkali-pectates and cellulose-xanthate); complex structures are, of course, attacked in various ways, the straws of cereals and esparto giving from 50—60 per cent. of soluble derivatives.

IV. With regard to hydration: the cellulose-xanthates, on decomposition, yield hydrates of remarkable properties. A 1 per cent jelly of the regenerated cellulose has the consistency of a jelly containing 5 per cent. of gelatin; even at a concentration of 0·25 per cent. cellulose there is a distinct appearance of gelatinisation in the solution.

The 10 per cent. coagulum of regenerated cellulose (hydrate) has a consistency enabling it to be worked freely with the knife. When cut into slabs and exposed to pressure between layers of absorbent material, it is entirely dehydrated, the sheets from the press showing no further loss of water on exposure to the air; this air-dried cellulose retains 10 per cent of "hygroscopic" moisture. The loss of moisture on heating takes place in a manner somewhat different from that of the fibrous-celluloses. In its anhydrous condition (dried at 105°), it may be considered as having the composition $4C_6H_{10}O_5,H_2O$.

The numerical results were as follows.

I. Specimens of Swedish filtering paper were converted into alkali-cellulose, and then into xanthate. The xanthate solutions were diluted to 5 per cent. strength (cellulose). From two specimens, the cellulose was regenerated without further treatment, (*a*) by spontaneous decomposition at 15°—18°, (*b*) by more rapid gelatinisation at 60°. To another specimen (*c*), sulphurous acid was added in the proportion of one-third the equivalent of the alkali present. This treatment gives a colourless solution of the cellulose compound, and, on standing, a colourless jelly of regenerated cellulose.

The cellulose, separated as above, was exhaustively purified from alkaline bye-products, and from residues of sulphur compounds by treatment with hypochlorite solution (NaOCl). It was then dried at the ordinary temperature for some days, finally at 105°, and weighed.

	Weight of original cellulose.	Weight of regenerated cellulose.
(*a.*)	1·7335	1·7480
(*b.*)	1·7415	1·7560
(*c.*)	1·8030	1·8350

Those results indicate a gain in weight of 1·1 per cent. From the formula $4C_6H_{10}O_5,H_2O$, which expresses the' results of analyses of the product, the calculated increase should be 2·7 per cent. The difference expresses a slight hydrolysis to soluble products, which no doubt falls on the oxycellulose present even in these purest forms of the normal fibre-celluloses. They result from the bleaching processes to which the raw materials have been subjected, and their presence is indicated by a small yield of furfural (0·2—0·4 per cent.) obtained on boiling with dilute hydrochloric acid (sp. gr. 1·06). The normal celluloses may, therefore, be said to be quantitatively regenerated from the thiocarbonate solutions.

2. Various celluloses of groups B and C (p. 439) were dissolved as xanthates. The solutions were allowed to decompose spontaneously, and the regenerated celluloses purified from bye-products. These celluloses were examined for furfural-yielding groups, which were found to be present in greatly diminished proportions. The following typical results may be cited.

	Furfural from original cellulose.	Furfural from regenerated cellulose.
Cellulose from Pinus (Group B) ..	5·5	2·0
„ „ Esparto („ C) ..	13·5	5·0

It seemed probable, however, that the furfural-yielding groups, in the process of conversion into xanthates, undergo hydrolysis forming soluble derivatives; this was found to be the case. The above results, therefore, do not complete the statistics of the reaction. The following quantitative study of esparto-cellulose in relation to the thiocarbonate reaction, shows conclusively (*a*) that the furfuroïds of these "natural oxycelluloses" are hydrolysed to soluble derivatives; (*b*) that they undergo changes—probably deoxidation—which result in a considerable diminution in the yield of furfural.

$$\overbrace{\text{Insoluble cellulose (80), yielding furfural = 2·0 per cent.} \qquad \text{Soluble derivatives (20), yielding furfural = 26·2 per cent.}}^{\text{Esparto cellulose (100) dissolved as xanthate gives on decomposition}}$$

From these numbers it will be seen that the furfural aggregate is $\frac{2·0 \times 80}{100} + \frac{26·2 \times 20}{100} = 6·84$ per cent., calculated on the original cellulose; whereas the cellulose in its original state was found to yield 13·6 per cent., a diminution of 50 per cent.

These results confirm the previous observations of our assistant, Mr. C. Smith, that the furfuroids of these gramineous celluloses are attacked by deoxidising agents (Trans., 1894, 65, 472), and are therefore probably oxyhexoses, and not, or only in part, pentosans (see *infra*).

3. Various compound celluloses were also studied in relation to this reaction as follows.

Lignocelluloses.—(*a.*) *Woods.*—Pine and beech, in fine shavings, were heated with excess of 15 per cent. solution of sodium hydroxide (NaOH), well drained and exposed to carbon bisulphide for various periods, extending to several days. The results may be taken as substantially *negative;* the characteristic xanthate reaction was in no case obtained.

(*b.*) *Jute.*—The fibre was prepared by a previous treatment with a strong solution of sodium hydroxide (12 per cent. NaOH) in the cold, washing, and drying.

The following results are typical.

10 grams of purified fibre, treated with excess of a 15 per cent. solution of sodium hydroxide, drained, and exposed during 24 hours to the action of carbon bisulphide (5 grams). On treating the product with water, the fibre swells to a jelly occupying 50—60 times the volume of the original. The jelly was separated from products actually in solution by considerably diluting it, and the dissolved products were precipitated by adding zinc acetate in excess. The precipitated zinc compounds, after washing, were treated with dilute hydrochloric acid. The final results were.

Fibre undissolved..........	73·65 per cent.
Products dissolved	25·60 "

The dissolved products were found to yield 0·118 gram furfural or 1·2 per cent. on the original. The "furfuroids" were entirely precipitated by the zinc salt, the filtrate from the precipitate of zinc compounds yielding no furfural on evaporating to dryness and distilling the residue with hydrochloric acid.

The residual fibre, left undissolved in the original treatment, yielded 4·1 per cent. of furfural. It is evident that the furfuroïds of the fibre are affected by the process, the "total furfural" being reduced by 50 per cent.

Furfural from original jute.	Furfural from products of thiocarbonate reaction.	
	Insoluble.	Soluble.
8·5 per cent.	3·0	1·2

Total calculated on original fibre = 4·2 per cent.

The result is similar to that obtained with the celluloses of the gramineæ (p. 443).

Cuticular Celluloses.—A specimen of raphia—which consisted of the epidermis of leaves of the *Raphia R.*—was treated with a 15 per cent. solution of sodium hydroxide, and afterwards with carbon bisulphide. The statistical results of the reaction were as follows.

Undissolved	60	per cent.
Dissolved and reprecipitated by acids	12	„
Dissolved and not reprecipitated by acids	28	„
	100	

These results indicate a direction in which the thiocarbonate reaction will be available for solving constitutional problems. In the pure celluloses, the alcoholic OH-groups predominate, and the conversion into soluble xanthate is complete. The compound celluloses, on the other hand, have more of the character of esters; the non-cellulose groups of the lignocelluloses, for example, have well-marked phenolic and quinonic characteristics, and their more acid OH-groups have combined with the alcoholic OH-groups of the original and unmodified cellulose groups. This union, the conditions of the xanthate reaction are unable to resolve, and the result affords a further proof that these natural products are not to be regarded as *mixtures* of celluloses and so-called encrusting matters (non-cellulose).

The hydration and dehyration of cellulose are characteristic features of the thiocarbonate reaction. The following observations on a solution of cellulose xanthate are typical. The solution which contained 5 per cent. of cellulose, was kept in a stoppered cylinder at the ordinary temperature of the air:

	Time in days.	Vol. of cellulose hydrate.	Diff. from 100 c c. = vol. expressed.
Coagulation	8th day	100 c.c.	—
First appearance of liquid	11th „	100 „	—
Gradual shrinkage of hydrate with expression of water	16th „	98·0 „	2·0 c.c.
	20th „	83·5 „	16·8 „
	25th „	72·0 „	28·0 „
	30th „	58·0 „	42·0 „
	40th „	42·8 „	57·2 „
	50th „	38·0 „	61·5 „

The shrinkage of a coagulum of cellulose (hydrate) containing 5 to 10 per cent., is gradual and uniform; at 10—12 per cent. there is a retardation of the shrinkage; and the 12—15 per cent. coagulum may be considered as a hydrate permanent in a moist atmosphere.

This product is endowed with considerable tenacity and elasticity;

cubical blocks of 1—2 cwt. may be freely handled in the 'rough and tumble' of industrial operations. The further treatment of this hydrate for the final preparation of the "air-dry" cellulose is carried out industrially as follows:

(1.) These blocks, 24″ × 18″, are cut down with a guillotine knife into slabs, which are washed to remove the alkali bye-products, (sodium carbonate, thiocarbonates, &c.), bleached, if necessary, by treatment with hypochlorites, and when thus purified are exposed to a pressure of 100—300 tons per square inch, between sheets of absorbent material (felts), the pressure being applied gradually. Under this pressure, the dehydration of the cellulose is virtually complete, the final product being a translucent film of regenerated cellulose; in the "air dry" condition, this cellulose retains 10 per cent. moisture, more or less, according to the temperature and dew-point of the surrounding atmosphere. A comparison of this film-cellulose with the original film-cellulose in regard to further loss of moisture on heating, established the following points:

Heated at.	Fibre-cellulose.	Film-cellulose.
90—100°	Rapidly lost 6·8 per cent., then remained constant.	Lost 8·6 per cent. more slowly than fibre cellulose.
100—120	Further loss of 0·5 per cent.	Further gradual loss of 3·9 per cent.
130—160	Further loss of 0·5 per cent. (attended by slight decomposition).	

The substances were heated in a current of carbonic anhydride, the moisture expelled being collected in a calcium chloride absorption tube.

These results are typical of innumerable observations made in the course of the industrial working of these products, and cover the essential features of the hydration and dehydration of cellulose in the complex of reactions presented by the xanthate reaction.

This hydration-history of cellulose has many analogies with the phenomena presented by the growing plant and the history of elaboration of permanent tissue. We merely call attention to the fact in order to draw the conclusion which it warrants, namely, that the progressive dehydration of the tissues which accompanies maturation depends in an important sense on the properties of the hydrates of cellulose, considered independently of the particular conditions of their association with the assemblage of products constituting the living plant.

Acetylation of Cellulose. New Method.

In examining the modification of cellulose as obtained from its solutions as xanthate, we were early impressed with its greater chemical activity as manifested, for instance, by its reacting with acetic anhydride at the boiling point of the latter. The resulting solution of acetate has, however, such extraordinary viscosity that the action is considerably impeded when the proportions of liquid to cellulose are less than 20 to 1 by weight. Even at this dilution the action is difficult to control: prolonged boiling is necessary, and there are evidences of secondary changes which invalidate the conclusions to be drawn from the composition of the product. We found, however, that the acetylation could be reduced to a reaction of great simplicity as follows:—

The regenerated cellulose (xanthate reaction) is thoroughly purified in the finely divided condition and mixed with zinc acetate in concentrated aqueous solution. The proportion of the latter to cellulose is that of the molecular ratio $C_6H_{10}O_5 : 2ZnAc_2$. The mixture is evaporated down on the water-bath with continual stirring, and when dry it is reduced to a fine powder; this is finally dehydrated by heating at 105—110° and is then gradually mixed in the cold with the equivalent of acetyl chloride: reaction ensues, the temperature being kept below 35° by suitable means. The product is drenched with glacial acetic acid after being warmed to promote solution of the acetate and the bye-products, the viscous solution is poured into water, and the gelatinous precipitate washed till free from zinc salts. It is then dried, the cellulose acetate dissolved in chloroform and the solution freed, by filtration or prolonged standing, from any unattacked cellulose; the product is finally isolated by evaporating the solvent. When this is carried out on a glass plate upon which an even layer of the solution is spread, the product is obtained as a brilliant colourless film of considerable tenacity.

When the precautions mentioned have been duly observed, the product has all the characteristics of a simple acetate of an unresolved cellulose; thus, on saponification, the cellulose is obtained as a "continuous" film, and on boiling with aqueous alkali (NaOH) and adding Fehling's solution, there is no reduction of CuO, either in the solution or on the film.

In certain cases, however, the acetylising action is attended by local or general rise of temperature. The product in such cases has very different characteristics. It gives comparatively brittle films which become disintegrated on saponification; yellow soluble products are obtained which reduce cupric oxide freely, and the regenerated "cellulose" has the properties of a hydro- or oxy-cellulose also reducing cupric oxide. This differentiation of the products is confirmed by the results of analysis: the brittle product gives numbers corresponding with an acetate higher than the tetracetate, $C_6H_6O(OAc)_4$: the normal product gives numbers, both for saponification and yield of cellulose, in general concordance with the above formula.

Before citing the analytical results, it is necessary to say a few words as to the methods employed. The most rapid and satisfactory process of saponification is that of boiling with normal sodium hydroxide diluted with its own volume of alcohol. The acidimetric estimations were in some cases confirmed by distilling off the acetic acid and estimating it in the distillate. The residual cellulose is digested with dilute acid, well washed, dried and weighed. The following results are typical.

		Acetic acid.		Cellulose.
		Acidimetric estimation.	Saponification and distillation.	
Products in coherent films. Cellulose regenerated of normal characteristics.	(1)........	72·4	—	43·6
	(2)........	73·1	69·2	43·2
	(3)........	73·3	—	44·0
	(4)........	68·0	—	50·0
Products giving brittle films. Cellulose in part hydrolysed on saponification; products reducing CuO.	(1)........	81·2	—	—
	(2)........	80·3 81·7	—	32·0
	(3)........	82·8	—	22·4

The quantities calculated are for the formula—

	Acetic acid.	Cellulose.
$C_6H_6O(OAc)_4$	72·7	49·1

It is, of course, impossible to formulate a more highly substituted cellulose derivative, and it is unnecessary to speculate as to the relationship of the higher acetates to the lower, or to the original cellulose. On the main question, the evidence is distinct. The further resolution of the problem will be undertaken with very much larger supplies of the products, which will soon be available, as the industrial preparation of the products is in course of arrangement.

By way of further elucidating the reaction of acetylation, and confirming the hypothesis on which the method was devised, other experiments were made. The most striking result was obtained with a mixture of the regenerated cellulose and urea. The mixture was prepared as in the case of the zinc salt: 6 grams of the cellulose (calc. dry) were stirred into a concentrated aqueous solution of 4 grams of urea, dried at 100°, and then dehydrated at 105—110°. This mixture reacted with the acetyl chloride similarly to the zinc acetate mixture, and satisfactory yields of the purified product were obtained, namely, from 10 grams of the mixture (*a*) 4 grams, and (*b*) 5 grams of products. These were analysed, with the following results.

	Acetic acid (saponification).			Cellulose.
(*a*)	67·4	67·3	68·0	47·0 per cent.
(*b*)		70·0		—

The function of the urea in determining the action, we regard as similar to that of the zinc oxide, that is combining with the acid groups of the cellulose molecule sufficiently to bring the alcohol OH-groups into freer play, and afterwards combining with the hydrogen chloride in the reaction.

Other bases, such as ammonia and hydroxylamine, give similar, but inferior, results, the action being much more limited than in the case of urea.

Some Electrolytic Phenomena of Cellulose (Hydrates).

Our observations began with an investigation of the insulating properties of films of cellulose obtained by the thiocarbonate process. We found them inferior in this respect to the fibrous celluloses in the form of paper, the insulation being approximately in inverse proportion to the normal hygroscopic moisture, namely 7 : 10.

As there are many phenomena connected with cellulose, and also many of its properties which indicate a species of saline activity, it was considered possible that it might behave as an electrolyte if water were present in larger proportion. The following experiments were made on the conductivity of moist cellulose as compared with that of water. A rag pulp was prepared, and after being exhaustively purified, it was diffused through distilled water, and the mixture poured into glass tubes, closed below with a diaphragm of muslin. The pulp was pressed down, and finally made into a compact cylinder by strong pressure. At each end a flattened coil of copper wire was placed in contact with the cylinder of moist pulp, the wires being brought through corks and connected with the terminals of a battery. Tubes of exactly similar dimensions and arrangement, containing distilled water only, were provided for comparative observation. The tests were made in the usual way with a reflecting galvanometer, the electromotive power being small dry cells, giving a current of about 1/20 ampère with an E.M.F. of about 1 volt. per cell.

	Battery.	Length of column.	Galvanometer.
(A.) *Water.*—			
	6 cells (series).	140 mm.	115°
	"	70 "	205
		35 "	410
(B.) *Moist pulp.*—			
	6 cells	(1) 140 "	300
		(2) 73 "	535
	1 cell	(3) 25 "	285

On reducing these numbers to unit length, and to unit E.M.F., it will be seen that they show a sufficiently close agreement, the numbers for the B series being 42 : 39 : 43. Approximately, therefore, the conductivity of the moist cellulose is three times that of a column of water equal to it in length, and of the same degree of purity as that used to moisten the pulp. The proportions of water to cellulose in the tubes of series B, it remains to add, were

	(1.)	(2.)	(3.)
Water	63	66·5	57·5
Cellulose	37	33·5	42·5

Having established the superior conductivity of moist cellulose, we may now describe experiments illustrating the electrolytic effects which mark the passage of the current through moist cellulose films, paper, cloth, &c., placed between metallic conductors. A convenient battery strength for producing the effects is a 4-cell "bichromate" battery; but a current of 1/30 ampère is sufficient with a difference of potential between the terminals of 3 to 6 volts.

Briefly and generally, the metal of the anode is dissolved, and carried forward into the cellulose where it is deposited in combination. Even gold is attacked; platinum also; but these metals are carried through the cellulose and deposited on the cathode. Gold, however, is, to a certain extent, retained. The results with silver are characteristic. The deposit is brownish, and is immediately decolorised by weak acetic acid; it is therefore oxide of silver. On reversing the current maintaining the contact, a secondary electrolysis is determined, and the oxide is converted into metal.

A quantitative observation may be cited as typical. A piece of pure Swedish filter paper was cut to a square 5 cm. on the side, and clamped between a silver (anode) and a copper plate. The current was passed for 60 secs. The silver deposited in the paper was 0·005 gram, which may be taken to represent a current of

1/12 ampère. The battery used was a 5-cell bichromate battery in a nearly exhausted condition.

The reactions with the other metals call for no particular description. We may mention copper which is deposited as a blue hydrated oxide; and tin as stannous oxide, which may be "developed in gold" by treatment with auric chloride. Zinc is peculiar, in that it is deposited in both directions of the current; that is, with a Zn | Pt combination of terminals, the cellulose contains zinc oxide, after the passage of the current, whether from Zn to Pt, or *vice versâ;* treatment with a neutral solution of hæmatoxylin develops a characteristic colour, the zinc from the anode being purple, whilst that from the cathode is blue.

More critical observations have been made showing that between the terminals there is a true electrolytic circuit, which is affected by the conditions of the circuit. Thus, in completing a Zn | Pt circuit through three folds of paper, the effects are obtained as above described; but in substituting for the central fold, paper containing 3·5 per cent. of zinc oxide, the zinc terminal taken as anode is not attacked. The zinc oxide being + to zinc counters the ordinary action of the current.

We do not propose to extend the discussion of these phenomena at the present time; they are the subject of systematic research, the results of which will be treated in a special communication.

It is necessary to mention that similar phenomena are shown by a diversified range of colloid substances, silk, wool, gelatin, and even asbestos; further, water is not necessary to the reactions. We have obtained similar results with other liquids similarly used, notably absolute alcohol.

In conclusion, without committing ourselves to any *theory* outside the evidence which we have accumulated, we may state that the results clearly indicate that the phenomena are the result of direct transmission of the current by the colloids, and not by associated saline impurities. The latter hypothesis has been exhaustively investigated, and the results obtained when ordinary saline electrolytes are present, are the exact reverse of those described, the ions taking the usual form and course, being separated upon their respective electrodes.

The subject is introduced as incidental to the general theoretical development of the chemistry of cellulose reactions. It is another link in the chain of demonstration of those characteristics of the molecule which, for want of a better term, we describe as "saline."

XLVIII.—*Potassium Nitrososulphate.*

By Edward Divers, M.D., F.R.S., and T. Haga, F.C.S.

Hantzsch has recently expressed the opinion (*Ber.*, 1894, **27**, 3264) that two potassium nitroxysulphites exist, one being Pelouze's nitrosulphate (the nitrososulphate of Henry Watts and of ourselves), the other a salt obtained by Raschig (*Annalen*, 1887, **241**, 230), and again by himself. This opinion we cannot share, for reasons we proceed to state.

Above all, Hantzsch is mistaken in his belief that Pelouze found the nitrososulphates to be precipitable by barium salts; Pelouze expressly states the contrary, advancing it as a proof that these salts cannot be taken to be sulphates with nitrous oxide acting merely as water of crystallisation. There is, indeed, a sentence in his paper calculated to mislead on this point, wherein he says that, with a barium salt, the solution of the "new salt" gives a precipitate which, when washed, is soluble in nitric acid. This precipitate, however, as the context clearly shows, is due to impurities, such as carbonate, in the potassium hydroxide employed, and he mentions it merely to show that the precipitate is free from sulphate. Thus, the property which Hantzsch regards as, above all, characteristic of Pelouze's salts, has no existence.

Hantzsch says, further, that there is a striking contrast between the ease with which his own potassium salt decomposes and the relatively great stability of Pelouze's salt, as the latter can be purified by recrystallisation from boiling water, with very little loss by decomposition, whilst his preparation in aqueous solution decomposes somewhat quickly, even at the common temperature, and with effervescence when gently heated.

Both of these statements, however, are true of one and the same preparation. We find from our experiments that the salt, as obtained in a strongly alkaline mother liquor, following Pelouze's directions, after having been thoroughly well drained on a tile, so as to be almost pure and without the least caustic taste, although still alkaline to litmus, can be purified, as Pelouze himself states, by dissolving it in the proper quantity of boiling water and quickly cooling the solution; there will, it is true, be brisk effervescence, but the greater part of the salt can be recovered, and will be found to be free from sulphate, after draining on a tile. Again, the pure salt can be dissolved in just sufficient boiling water, with but little effervescence, if a few drops of dilute solution of potassium hydroxide has been previously added to the water, and can be recovered with very small loss if the hot solution is quickly cooled by immersion in cold water. The crystals deposited may then be redissolved in their mother liquor, and the solution brought to full ebullition over a naked flame, and yet much of the salt be recovered, provided the solution is quickly cooled. Further, if water at 50° is used each time, even if no alkali at all be present, the pure salt may be dissolved and recrystallised four times over, the crystals being collected and drained from the mother liquor each time; there is here, however, great loss from one cause and another, a fraction of a gram only being obtained from 10 grams after four crystallisations. Now, such a salt as this, fully coming up, as it does, to every expectation based on Pelouze's description, will effervesce freely if its solution is heated to 60° or above, and will decompose entirely in a day or two, even at the ordinary temperature, thus behaving in accordance with Hantzsch's description. Pelouze, we may add, found that the less stable ammonium nitrososulphate decomposed slowly in solution even at 0°, and quickly with effervescence at 40°.

Another point of contrast noticed by Hantzsch in the effect of heat on the two salts is that the salt he prepared is gradually but completely decomposed into sulphate and nitrous oxide when heated up to about 90°, whilst Pelouze states that he found his salt neither lost weight nor decomposed at 110—115°. We find that the salt prepared by us behaves conformably with Hantzsch's account, and feel ourselves justified in setting down Pelouze's statement to the contrary to some oversight on his part, for we are unable to confirm Hantzsch's opinion of Pelouze's accuracy in the description he gives of his salts.

We here give the results of the observations we have made. At the bottom of a test-tube, immersed in oil, the pure salt, on two occasions, exploded at 91°, when heated in well-dried air. In a capsule in the ordinary air bath, some of the same pure salt reached 108° before it exploded. Again, at the bottom of a test-tube in oil, in a gentle current of well-dried hydrogen, the salt exploded also at 108°. The decomposition is an exothermic one, and we are disposed to attribute this difference in the temperature of explosion to the well-known great cooling effect of hydrogen, being about equal in the test-tube to that of the use of an open vessel in a capacious air bath, rather than to the exclusion of air by the hydrogen. In another experiment made in dried hydrogen, the salt lost only 10 per cent., that is, half the total possible loss of weight when heated 2¼ hours, at 95°, and the whole, or 20 per cent., not until the salt had been heated 12 hours. Thus, the loss in weight is slow, and if a higher temperature (107°), mistaken for 110°, had been maintained for only a few minutes, it would have had so small an effect as, probably, to have deceived Pelouze. When the salt does suddenly decompose, there is a marked rise of temperature, and this may have caused him to name 130° as the decomposition point. Even if these suggestions are rejected, and Pelouze's statement is taken as correct, this difference in behaviour to heat is the only one between Hantzsch's and Pelouze's preparations.

From Pelouze's account it is to be inferred that, while in presence of moisture and acids, potassium nitrososulphate decomposes into potassium sulphate and nitrous oxide, it is converted by dry heat wholly into sulphite and nitric oxide; Hantzsch, on the other hand, finds that by dry heat not more than 20—26 per cent. of the salt is changed into sulphite and nitric oxide, the rest becoming sulphate and nitrous oxide. There is nothing, however, to show that Pelouze worked quantitatively in the matter. Besides, Hantzsch himself has found that silver potassium nitrososulphate does wholly decompose into sulphite* and nitric oxide by heat, thus greatly lessening the weight that might be attached to this supposed difference.

On heating the salt in dried hydrogen until it exploded at 108°, we got results showing that 28·2 in one case and 29 parts per 100 in another case had been changed into sulphite. Our mode of working, however, was not only a little different from that adopted by Hantzsch, but we had to estimate the nature of the change in another way. He exploded the salt, and noted its loss in weight, and from this calculated how much of it had given off nitric oxide and how much nitrous oxide. We could not do this, since much of the residue was always blown out of our tube. Instead, therefore, we determined by the iodine method the amount of sulphite in a weighed quantity of the residue; there was always a trace of nitrite present.

We have now noticed all the points of supposed difference between Pelouze's nitrososulphate and what Hantzsch has designated the Raschig salt, and that the explanations we have offered, taken in conjunction with the experiments we have made, are sufficient to show that the two salts are one.

We will now return to Raschig's other salt.

This salt, which Raschig and Hantzsch have erroneously taken to be identical with Pelouze's potassium nitrososulphate, has two specific characters—it gives a barium salt insoluble in water, and it yields dipotassium oximidosulphonate when its solution in weak potash is made to crystallise, either by cooling or by evaporation. It may be mentioned here, parenthetically, that we have found it impossible to get any oximidosulphonate from pure potassium nitrososulphate. To get his salt, Raschig passed nitric oxide through potassium sulphite and evaporated the solution over sulphuric acid until crystalline crusts formed. The product obtained by other workers has always been that which crystallised out during the absorption of the gas.

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* Impressed by the stability of silver potassium sulphite, Hantzsch is led to recognise in it that constitution which one of us and Shimidzu, unknown no doubt to him, had long since given it (this Journal, 1882, **49**, 581). Further, that it is like the mercury sulphites, which, according to Barth, he says, are sulphonates. We not only agree with this view of the constitution of these salts, but would point out that Barth, in the paper quoted by Hantzsch, fully credits Divers and Shimidzu with that view, and then adopts it and confirms it.

Hantzsch has tried in vain in various ways to prepare this salt. As for ourselves, in whatever way we have worked, we have always got Pelouze's nitrososulphate, and no other along with it, whether we used a freezing mixture of ice and salt, the temperature of melting ice, or the ordinary atmospheric temperature, whether we had much potassium hydroxide present or none at all, worked for abundant yields of salt from the first, or stopped before crystals began to form, and then evaporated the solution over sulphuric acid, or, lastly, evaporated the mother liquors from the first-formed crystals.

Potassium nitrososulphate we find to be soluble in a little more than eight parts of water at 14½°, but it is less soluble in presence of potassium hydroxide. Even in the absence of alkali it can readily be recovered by evaporating its solution over sulphuric acid, although not without loss.

In composition, so far as potassium and sulphur are concerned, which alone were estimated by Raschig, this nitroxysulphite of his agrees very nearly with his "basic potassium dihydroxylamine sulphonate" (*op. cit.*, p. 192) if undried. From that salt, too, it appears to be indistinguishable by any properties, save an inconstant one. Raschig says that on several occasions this nitroxysulphite gave off some nitrous oxide on being dissolved in hot weak potash solution; as, however, Pelouze's salt would behave in the same way, it is not improbable that it may have been occasionally mixed with the latter in the crystalline crusts Raschig obtained by evaporating his solution. Otherwise, both the dihydroxylamine salt and this nitroxysulphite, even in dilute solution, give a barium precipitate soluble in acids, the solution quickly depositing barium sulphate. Both salts, it must be inferred, freely evolve nitrous oxide when acidified, and both are decomposed by water, and then yield oximidosulphonate.

Reserving for future publication all details, we may state now that oximidosulphonates and also salts similar to, if not identical with, Raschig's dihydroxylamine salt, are very easily obtainable from potassium sulphite and nitrous fumes. Even with nitric oxide, unless very special precautions are taken, at least minute quantities of dipotassium oximidosulphonate are always formed, and can be separated by evaporating the mother liquors of potassium nitrososulphate with care almost to dryness, sometimes with the addition of alcohol; if precautions are not taken to keep the nitric oxide colourless and all air absent, the oximidosulphonate forms quickly in notable quantity. The question arises, did Raschig take these precautions? Although it may be assumed that he did, there is nothing in his memoir to show that he was aware of this cause of error, or that he took any such precautions as, for instance, were taken by Hantzsch to have his nitric oxide pure. Until some definite method of preparing Raschig's isomer of Pelouze's potassium nitrososulphate is described, its existence is a matter of doubt, especially when it is considered that Pelouze's salt mixed with some such salt as his own potassium dihydroxylaminesulphonate would have the properties of this isomeride.

In a short notice to the Society, entitled "The Existence of Barium and Lead Nitrososulphates" (Trans., 1885, **47**, 364), we communicated the fact that, although the alkali nitrososulphates had appeared hitherto to be incapable of undergoing ordinary double decompositions with other salts, we had found them capable of a few such changes, resulting in the precipitation from concentrated solutions of a barium and of a lead salt. No quantitative analysis of these salts was given. It was also there mentioned by us that silver nitrate, unlike copper sulphate, does not at once cause decomposition of alkali nitrososulphates. Now, Hantzsch, in his account of the preparation of barium potassium and silver potassium nitrososulphates, although he refers to the note above mentioned, does so merely in order to say that, according to us, salts of the heavy metals cannot be prepared; this is not only the reverse of our statement, but he ignores the existence of the two salts we mentioned.

A new point about nitrososulphates which, small in itself, may yet prove of significance in settling their constitution, is that their aqueous solution becomes strongly alkaline to litmus, phenolphthaleïn, or rosolic acid, soon after alcohol is added to it. No effervescence on standing, otherwise a marked phenomenon, is then observable, and the disappearance of the salt is greatly retarded, probably as an effect of the alkalinity induced in the solution, possibly also through presence of the alcohol itself. Neither sulphite, nitrite, nor oximidosulphonate is produced.

Both Pelouze and Hantzsch describe potassium nitrososulphate as being perfectly neutral to litmus. In this we differ from them. It is indeed so towards phenolphthaleïn and to rosolic acid, but to litmus, almost on first contact with it, the moist salt is alkaline, and its dilute solution becomes so in a few seconds. The salt tested by us had, in one case, been four times recrystallised from pure water. Besides, when such salt of alkaline reaction had all decomposed, either slowly in the cold or more quickly at a boiling heat, or in the cold by contact with spongy platinum, the product was always quite neutral potassium sulphate, thus showing the absence of any excess of alkali as impurity in the original salt.

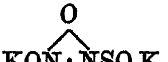
The knowledge of the constitution of the nitrososulphates seems to stand just where it did ten years ago, when we were led to see in these salts the presence of the radicle $-SO_2OK$, a view which has met with general recognition since, if we except some hesitation about its acceptance on the part of Michaëlis (*Graham-Otto's Anorg. Chem.*, **4**, 1515). Raschig in adopting it, two years later, fully stated that it was ours, but Hantzsch, although referring to Raschig's views, has overlooked that fact. In proposing at that time a new formula for these salts, we did not venture to resolve the nitroxy-radicle, and wrote $K(N_2O_2)SO_3K$, just as Traube is temporarily doing with his isonitramines. At the present time, we are disposed to adopt, as the legitimate outcome of the reduction of these salts into hyponitrites and sulphites, the expanded formula $K{\cdot}ON{:}NO{\cdot}SO_3K$, according to which nitrososulphates are simple sulphates of the radicle $M{\cdot}ON_2-$ (where M is a univalent metal or ammonium).

There are three objections which can be raised to this conception of their nature. One, made by Pelouze 60 years ago, may be stated almost literally in his words. Is it probable that nitrous oxide, contained as such in these salts, can, by the small rise of temperature which causes it to become nitric oxide, take oxygen from such a stable compound as sulphuric acid? We reply that, since the oxygen which has converted sulphite to sulphate has not, in doing so, parted from the nitrogen of the nitric oxide, it may well enough be expected to keep it when, by a sufficient elevation of temperature, the complex molecule of the salt has to break up, though even then, as at lower temperatures, some of it does leave nitrogen in order to remain in the sulphate.

Another objection to these salts being considered as sulphates, which may suggest itself, as it also did to Pelouze, is that they give no precipitate of sulphate with barium chloride. But this may only show that they resemble alkyl sulphates, such as the sulphovinates; whilst the instantaneous precipitation of barium sulphate on the addition of an acid confirms the view as to their sulphate constitution, since all known sulphazotised salts of the sulphonic type, when acidified, take a notable time before barium sulphate begins to precipitate, brief though that time, during which hydrolysis is taking place, may be in the case of the trisulphonated nitrile salts.

A third and obvious objection to the view that nitrososulphates are true sulphates is that they resist decomposition by alkalis. It is here admitted that a constitution in which nitrogen is shown in direct union with sulphur would furnish, *primâ facie*, a more satisfactory ground for this stability than one in which it stands only in oxylic union with the sulphur. However, it should be considered that potassium ethyl sulphate, for example, shows some of that stability characteristic of potassium ethylsulphonate towards alkalis, although in it also, there is no immediate juxtaposition of ethyl to sulphur. But the special point for consideration is one which, as in so many other cases, structural formulæ fail to indicate. To take the commonest and simplest example, structural formulæ fail to account for the fact that the hydrogen of HO·K is so different in its chemical relations from that of $HO\cdot NO_2$. The point then is that, because sulphur is dibasic in nitrososulphates as in sulphites and sulphates, potassium nitrososulphate is a salt quite stable towards potassium hydroxide, though extremely unstable towards acids. The sulphur acts, so to speak, through or across the dinitrosyl on the potassium just as it acts in sulphates across the intervening oxygen, or as chlorine acts across oxygen as a monobasic radicle in chlorates, or phosphorus in phosphates as a tribasic radicle.

That nitrososulphates should decompose into sulphates and nitrous oxide, and also by sodium be reduced to hyponitrites and sulphites, is made very evident by the constitution here assigned to them.

Hantzsch's formula for these salts,  $\mathrm{KO}\overbrace{\mathrm{N}\cdot\mathrm{N}}^{\mathrm{O}}\mathrm{SO_3K}$, is perhaps preferable to ours for accounting for the stability of nitrososulphates towards alkalis. On the other hand, it affords no explanation of their instantaneous decomposition by acids, whilst their reduction by sodium becomes a very complex matter. Raschig's formula, $ON\cdot N<^{OK}_{SO_3K}$, would be almost equally good, were it not designed to show a possible decomposition into oximidosulphonate and nitrous oxide.

Traube (*Ber.*, 1894, **27**, 1507) thinks there is analogy between his isonitramines and the nitrososulphates, but we doubt very much whether any substantial anology will be established between them. It is true that both classes of compounds are metallic salts formed from nitric oxide, but then, as Traube has already shown, one of the nitrogens is united to the alkyl radicle of the isonitramine, whereas, as we have just pointed out, what little evidence there is shows that one of the atoms of oxygen, and not of nitrogen, is directly united to the sulphuryl. Again, in the formation of nitrososulphates, nitric oxide simply combines with a salt, whilst in that of isonitramines it unites a salt with more metal. In the formation of nitrososulphates, the presence of alkali, essential in the case of isonitramines, may be dispensed with, as was recognised by Pelouze as regards the ammonium salt, and as has been more conclusively ascertained by us in the case of the potassium salt.

Imperial University,
Japan.

XLIX.—*Contributions to our Knowledge of the Aconite Alkaloïds.* Part XI. *The Constitution of Aconitine. Acetyl Derivatives of Benzaconine and Aconitine.*

By Wyndham R. Dunstan, M.A., F.R.S., and Francis H. Carr, Salters Company's Research Fellow in the Research Laboratory of the Pharmaceutical Society.

In previous communications (Parts IX and X, Trans., 1894, **65**, 176 and 290), the authors showed that when aconitine is heated at its melting point forming pyraconitine, or when partially hydrolysed forming benzaconine, or when it is completely hydrolysed forming aconine, a molecular proportion of acetic acid is separated; from this it follows that aconitine must be regarded as a monacetyl derivative, namely, acetylbenzoylaconine ($C_{33}H_{45}NO_{12}$).

During the past year, experiments have been made with the view of re-forming aconitine from benzaconine by introducing an acetyl group into it, and thus confirming the correctness of the constitution deduced from analytical evidence. Although the acetylation of benzaconine has been carried out under various conditions, it has not, so far, been possible to prepare aconitine; diacetyl, triacetyl, and tetracetyl derivatives being formed, which are non-poisonous. Up to the present, no monacetyl derivative of benzaconine isomeric with aconitine has been obtained.

Diacetylbenzaconine, $C_{31}H_{41}(CH_3CO)_2NO_{11}$. This compound is prepared by acting on benzaconine dissolved in chloroform with a small excess of acetic anhydride at the ordinary temperature. It is an amorphous base insoluble in water, but easily soluble in ether or chloroform. The hydrobromide crystallises readily from alcohol on adding ether to the solution. It is found that when rapid crystallisation is caused by the copious addition of ether, the substance melts at 214°, but when crystallised slowly it melts at 265°. We have had occasion to draw attention to a similar behaviour of the salts of other alkaloïds of this group.

This derivative, apparently, is not toxic, and could not be made to yield a toxic alkaloïd by slow hydrolysis either with alkali or water, the product first formed in the former case being aconine, and in the latter benzaconine. The amount of acetic acid eliminated on hydrolysis was estimated, and found to be 16·2 per cent.; the quantity required by diacetylbenzaconine hydrobromide is 15·6 per cent. The method of hydrolysis employed in this case, as in all of those to be described, consists in dissolving a weighed amount of the substance in pure alcohol, adding pure sodium hydroxide solution, and then heating to 70°. An hour is sufficient to complete the action. The solution, after being nearly neutralised with dilute sulphuric acid, is evaporated (and in this particular case the haloid acid was removed by precipitation with silver sulphate). It is next repeatedly distilled with dilute sulphuric acid until no more volatile acid is obtained; the distillate is then shaken with benzene to remove benzoic acid, and titrated with N/20 soda solution.

Triacetylbenzaconine, $C_{31}H_{40}(CH_3\cdot CO)_3NO_{11}$.—This derivative is obtained by acting on a chloroform solution of benzaconine with acetic anhydride at 100°, or at the ordinary temperature in the presence of sodium acetate. It is crystalline, melts at 255—256°, and dissolves in alcohol and in ether, but not in water. Neither the base nor its salts produce any tingling when applied to the tongue, and, apparently, are not poisonous in small doses.

When completely hydrolysed with alkali, this substance furnishes aconine, benzoic acid, and acetic acid. The amount of acetic acid produced is 24·4 per cent., which agrees with the quantity required for a triacetyl derivative, namely, 24·6 per cent.; a diacetyl derivative requires 17·4 per cent. and a monacetyl derivative 9·27 per cent. Experiments were made on the partial hydrolysis of this base in the hope of obtaining a monacetyl derivative, but they were unsuccessful.

This triacetyl derivative appears to be the same as that described by Messrs. Freund and Beck (*Ber.*, 1894, **27**, 7321) as a monacetyl derivative. These observers, however, relied entirely on the results of combustions in determining the composition, and, as is well known, this is fallacious in cases like the present one, where the addition or removal of an acetyl group makes but little difference in the percentage composition. From the calculated percentages of carbon and hydrogen for monacetyl, diacetyl, and triacetyl derivatives tabulated below, it will be seen that even between the mono- and tri-substitution derivatives the percentage differences are small, whilst, on the other hand, the large differences in the percentages of acetic acid furnished by the hydrolysis of these substances affords a safe criterion of the number of acetyl groups which have been introduced.

$C_{31}H_{42}(CH_3{\cdot}CO)NO_{11}$. C = 61·20; H = 6·95; acetic acid = 9·27 per cent.

$C_{31}H_{41}(CH_3{\cdot}CO)_2NO_{11}$. C = 60·96; H = 6·82; acetic acid = 17·41 per cent.

$C_{31}H_{40}(CH_3{\cdot}CO)_3NO_{11}$. C = 60·74; H = 6·70; acetic acid = 24·62 per cent.

When acetyl chloride is used as the acetylating agent in place of acetic anhydride, a different product is obtained. By allowing the chloride to stand for some hours with benzaconine, or one of its salts dissolved in chloroform, and then regenerating the base from the saline residue by means of dilute ammonia and extracting with ether, a crystalline base was obtained which melted at 162°. This is insoluble in water, and does not dissolve readily in dilute acids. The *hydrobromide* is crystalline, and melts at 231° after re-crystallisation from a mixture of alcohol and ether. The *aurichloride*, which is amorphous, contains 16·6 per cent. of gold.

Great difficulty was experienced in deciding as to the composition of this substance. It is not easy to dry it completely in a desiccator, and on prolonged heating at 100° it suffers some decomposition; concordant results, therefore, were not obtained on combustion. When dried for three hours, it lost about 4 per cent. of water, and on complete hydrolysis with alkali it furnished 25·8 per cent. of acetic acid, in addition to benzoic acid and aconine. The substance would seem, therefore, to be a tri-hydrate of triacetylbenzaconine, but this constitution cannot be regarded as established. It is not toxic in small doses, and no monacetyl-derivative could be obtained from it by partial hydrolysis.

Tetracetylbenzaconine, $C_{31}H_{39}(CH_3CO)_4NO_{11}$.—We have previously pointed out that aconitine forms an aurichloride of the usual type. Benzaconine, however, which is formed from aconitine by the hydrolytic separation of its acetyl group, furnishes a remarkable colourless aurichlor-derivative, $C_{31}H_{42}(AuCl_2)NO_{11}$, and from this it would appear that the atom of hydrogen in benzaconine which is replaced by the residue $AuCl_2$ is the same as that which is replaced by an acetyl group in aconitine. It seemed probable, therefore, that if the group $AuCl_2$ in this compound were replaced by acetyl, aconitine would be formed. It was found, however, that reaction between the gold salt and acetyl chloride does not readily take place; at 100° in a closed tube, on the other hand, the aurichlor-derivative is decomposed, and from the residue a crystalline base is obtained melting at 211°. It is insoluble in water, but dissolves in alcohol and in ether; dilute acids dissolve it with great difficulty. The same substance may be obtained by heating benzaconine with acetyl chloride, in a closed tube at 100°. It is not poisonous, and is remarkable in forming a colourless aurichlor-derivative (m. p. 225°) containing 18·2 per cent. of gold. As, on hydrolysis, this base furnishes 33·8 per cent. of acetic acid, besides benzoic acid and aconine, it appears to be a tetracetylbenzaconine, the aurichlor-derivative of which would contain 18·8 per cent. of gold, and would furnish 31·16 per cent. of acetic acid on hydrolysis.

It will be seen from these results that it has not been possible to prepare a monacetylbenzaconine corresponding with aconitine, whilst the higher acetyl derivatives which have been prepared differ from aconitine in not being highly poisonous. The exact physiological action of these derivatives is being investigated by Professor Cash, F R.S., of Aberdeen.

We proceeded, in the next place, to determine whether we could prepare triacetylbenzaconine and tetracetylbenzaconine, taking aconitine as a starting point instead of benzaconine. Aconitine being acetylbenzaconine, its diacetyl-derivative should correspond with triacetylbenzaconine and its triacetyl-derivative with tetracetylbenzaconine.

Acetic anhydride does not react with aconitine, even after prolonged standing or heating at 100°.

Triacetylaconitine.—When acetyl chloride in large excess is allowed to act on aconitine at the ordinary temperature during a day, in the absence of a solvent, a crystalline base may be extracted with ether in the usual manner. It melts at 207°, and crystallises in fine needles from its alcoholic solution, especially after the addition of ether, in which it is sparingly soluble. It dissolves with difficulty in dilute acids. and its salts are unstable. On combustion this substance furnished the following data.

0·2068 gave 0·4572 CO_2 and 0·1314 H_2O. $C = 60·30$; $H = 7·06$ per cent.
$C_{33}H_{42}(CH_3{\cdot}CO)_3NO_{12}$ requires $C = 60·54$; $H = 6·59$ per cent.

On hydrolysis, this base furnished aconine, benzoic acid, and 31 per cent. of acetic acid; an amount which corresponds with the calculated quantity for triacetylaconitine (31·16 per cent.).

In addition to this substance, a small quantity of another, and apparently non-basic, compound is formed by the action of acetyl chloride on aconitine, but this was not further examined.

This triacetylaconitine is isomeric, and not identical with the tetracetylbenzaconine, described above. Not only do these two substances differ in physical properties, but the former compound has the characteristic physiological action of aconitine, whilst the derivative prepared from benzaconine has not.

Diacetylaconitine.—This compound was prepared by acting with acetyl chloride on aconitine, or on one of its salts, either in the dry state or dissolved in chloroform for several hours at the ordinary temperature. It is a crystalline base melting at 158°, only slightly soluble in water, but readily in alcohol or chloroform, less so in ether. The combustion of the base furnished the following data.

0·1775 gave 0·3974 CO_2 and 0·1126 H_2O. C = 61 06; H = 7·05.
0·1607 „ 0·3607 CO_2 „ 0 1607 H_2O. C = 61·21; H = 7·01.
0·1884 „ 0·4191 CO_2 „ 0·1208 H_2O. C = 60·67; H = 7·11.
$C_{33}H_{43}(CH_3{\cdot}CO)_2NO_{12}$ requires C = 60·74; H = 6·7 per cent.

If auric chloride is added to a solution of the hydrochloride of this base, a yellow, amorphous precipitate is thrown down, and when this is dissolved in alcohol and crystallised by adding a mixture of ether and light petroleum, fine, white needles (m. p. 164°) of an aurichloro-derivative are obtained. The following are the results of an analysis of this compound.

0·1683 gave 0·0318 Au and 0·0434 AgCl. Au = 18·89; Cl = 6·29.
$C_{33}H_{42}(CH_3{\cdot}CO)_2AuCl_3NO_{12}$ requires Au = 19·65; Cl = 7·08 per cent.

On alkaline hydrolysis, the base yielded aconine, benzoic acid, and 25·58 per cent. of acetic acid; the calculated quantity for diacetylaconitine is 24·62 per cent.

The physiological action of diacetylaconitine probably resembles that of aconitine, since it produces the characteristic tingling sensation. In this respect, as well as in physical and chemical properties, it differs from its isomeride triacetylbenzaconine.

Triacetylpyraconitine.—When pyraconitine hydrochloride, dissolved in chloroform, is acted on in the cold with acetyl chloride, a crystalline base melting at 204° is produced; it is insoluble in water, but dissolves in ether and in alcohol. This substance does not appear to be toxic. On combustion it furnished the following data.

0·1863 gave 0·4394 CO_2 and 0·1318 H_2O. C = 64·32; H = 7·8.
0·1807 „ 0·4214 CO_2 „ 0·1288 H_2O. C = 63 60; H = 7·91.

The mean percentages are C = 63·92, H = 7·85, which are in fair agreement with those calculated from the formula

$$C_{31}H_{40}(CH_3{\cdot}CO)_3NO_{10},$$

which requires C = 63 8; H = 6·47 per cent. On hydrolysis, it afforded 22·6 per cent. of acetic acid, whilst the percentage calculated for the above formula is 88·02 per cent.

This derivative corresponds more closely with those of benzaconine than with those of aconitine, especially in not possessing the characteristic physiological action of the derivatives of the latter alkaloïd.

So far, then, all attempts to convert benzaconine into aconitine have failed, the other methods of acetylation which were employed having given negative results. The distinct characters, especially the different physiological action of the two sets of corresponding derivatives from benzaconine and aconitine, are somewhat difficult to understand, and the exact constitution of aconitine and its relation to benzaconine is a problem which still requires further elucidation.

We are unwilling to enter again into a discussion of priority with Messrs. Freund and Beck as to the establishment of the new view of the constitution of aconitine, but the fresh reply to our claim which Herr Freund (*Ber.*, 1895, **28**, 192), after the lapse of a year, has been led to make, renders it necessary for us to call attention to the facts of the case.

In the Proceedings of this Society recording the meeting of January 18, 1894, three short papers of ours were printed to which Herr Freund has made very misleading references. The first proves that the alkaloïd once obtained by Wright from aconite root, and called "Picraconitine," is not a pure substance, but consists chiefly of "Isaconitine," which we had previously shown to be *benzoylaconine** (Trans., 1893, **63**, 448). The second paper shows that when aconitine is heated at its melting point it loses one molecular portion of acetic acid, forming a new alkaloïd, pyraconitine. The third paper proves that acetic acid is formed, both when aconitine is converted into "isaconitine" by heating its salts with water, and also when aconitine is completely hydrolysed with formation of aconine, and, therefore, that it is probable the acetyl group of aconitine may be separated under both these conditions. Now the percentages of carbon and hydrogen in "isaconitine" represented by the old formula $C_{33}H_{45}NO_{12}$, or by the new formula $C_{31}H_{43}NO_{11}$, and also in aconine, using the two corresponding formulæ $C_{26}H_{41}NO_{11}$ and $C_{24}H_{39}NO_{10}$ are so nearly the same that proof as to the separation of one acetyl group from aconitine could not be obtained from the results of the ultimate analysis of these products; the elimination of the acetyl group making but little difference in the percentage composition.

$$\text{Benzaconine}\ \left\{\begin{array}{l}C_{33}H_{45}NO_{12}\ \text{(old formula)}\ C = 61{\cdot}20;\ H = 6{\cdot}95.\\ C_{31}H_{43}NO_{11}\ \text{(new formula)}\ C = 61{\cdot}48;\ H = 7{\cdot}10.\end{array}\right.$$

$$\text{Aconine}\ \ldots.\ \left\{\begin{array}{l}C_{26}H_{41}NO_{11}\ \text{(old formula)}\ C = 57{\cdot}46;\ H = 7{\cdot}55.\\ C_{24}H_{39}NO_{10}\ \text{(new formula)}\ C = 57{\cdot}48;\ H = 7{\cdot}78.\end{array}\right.$$

The required proof, however, could be gained by estimating accurately the proportion of acetic acid separated in these changes. Now, on attempting to estimate exactly the quantity of acetic acid formed under these conditions, we met with unexpected difficulties, so that, at the time these short papers were written, quantitative estimations of the desired degree of accuracy had not been made. On this account, we were unable to do more than indicate the nature of the conclusions at which we had arrived, and, for the same reason, we were obliged to retain the old formula for "isaconitine" in the first paper.* To have done otherwise would have been to anticipate the proof which could only be gained by exact quantitative determinations of acetic acid not, at that time, made; but we pointed out at the close of the third paper that if this view "should prove to be correct the nomenclature and formulæ of aconitine derivatives will need entire revision."

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* Until the simultaneous production of molecular equivalents of "isaconitine" and acetic acid had been established, it is clear that the experimental evidence strongly supported the hypothesis of isomerism.

Wishing to complete this proof by making the necessary determinations of acetic acid, we only presented to the Society two full papers for the Transactions, holding over the third until these determinations had been made. In about a fortnight, these estimations were finished, and they proved that exactly one molecular proportion of acetic acid separates when aconitine changes into "isaconitine" or into aconine. Therefore, aconitine must be, as we had indicated in our third short paper, mentioned above as published in the Proceedings, an acetyl derivative which loses its acetyl group under these conditions.

The *Berichte* issued from Berlin on February 19, 1894 (p. 433) contained a short paper by Messrs. Freund and Beck, their first contribution to the literature of aconitine, in which they stated that aconitine yields acetic acid on hydrolysis, but gave no estimations of the amount of acetic acid formed, or, indeed, any experimental proof of their assertion that aconitine is acetylbenzoylaconine. That they had seen our papers in the "Proceedings" is evident, from the fact that they actually quote from the first on "picraconitine," although they entirely ignore the two following papers, which not only indicate the conclusion they bring forward, but also supply experimental evidence of its truth. This proceeding seemed to us so unfair that we at once sent to the President of the Society a short statement of our quantitative determinations, at the same time drawing his attention to the paper of Messrs. Freund and Beck. The President directed that this statement should be included in the March number of the Journal (1894), then passing through the press, in which the first two papers had already been printed.†

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* Herr Freund has put an entirely erroneous interpretation on this circumstance.

† Having looked into the facts of the case this course had my entire approval.—EDITOR.

This third paper contains the only complete proof which has hitherto been adduced that aconitine is *acetylbenzaconine*, and it will be seen that it furnishes the results of estimations of acetic acid which, it was stated in our short paper published in the Proceedings nearly two months before, were in the process of being made.*

At the same time we sent to the German Chemical Society a statement of our claim for priority, which was printed in the *Berichte* of March 19, 1894 (p. 664). In his first reply to this statement,† Herr Freund (*Ber.*, 1894, **27**, 720) attempts to justify the absence of any allusion by him to our short papers in the Proceedings, on the ground that the production of acetic acid had already been observed by Messrs. Ehrenberg and Purfürst in 1892, and that the work of these observers formed the basis of his inquiry.

Now Ehrenberg and Purfürst had boiled aconitine with water, and stated that they had identified in the product benzoic acid; methyl alcohol; an acid, *probably* acetic acid; probably formic acid, together with the alkaloïds named (but neither described nor analysed) "picraconitine" and "napelline." They conclude, without quantitative proof, that *aconitine first loses benzoic acid, forming picraconitine*, then that picraconitine loses methyl alcohol, forming napelline, and, lastly, that napelline loses acetic acid, forming aconine. Messrs. Freund and Beck profess that it is these manifestly erroneous observations and conclusions which have led them to the very different result that aconitine is acetylbenzoylaconine, and that it loses acetic acid but not benzoic acid, forming "picraconitine." As a matter of fact, they reject every observation and conclusion arrived at by Ehrenberg and Purfürst, except the suggestion that acetic acid is probably a product of the decomposition of aconitine; that it is so was proved for the first time by us, and its true bearing indicated in our two short papers; to these Messrs. Freund and Beck do not even refer, although they were published more than a month before.

With this plain statement of the facts of the case we can confidently uphold our claim to priority against Herr Freund's criticism.

Messrs. Freund and Beck have proposed to alter to $C_{34}H_{47}NO_{11}$ the formula of aconitine which we give as $C_{33}H_{45}NO_{12}$, and Herr Freund professes to be aggrieved that we have not so far considered his proposal.* As a matter of fact, any discussion at the present time as to the exact formula of aconitine must be futile, as, until simpler derivatives of aconitine have been prepared and analysed, the question must remain, to a large extent, an open one. At the same time, we may state that analyses of the aconitine derivatives recently prepared by us do not furnish any ground for adopting the formula which Herr Freund has prematurely advanced; on the contrary, they lead us to prefer that long ago proposed by ourselves (see Proc., February 18, 1895). This will be made clear by an inspection of the following table.

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* The circumstances under which the third paper was published prevented us from including in it the full discussion of our results which we had previously intended it to contain, and it is obvious that through inadvertency the formulæ for aconine and its derivatives are incorrectly printed in the table at the close of this paper, but they are correctly given in the text immediately above.

† Herr Freund states that he has not replied until now (*Ber.*, 25, Feb., 1895, p. 192), but a reference to his paper in the *Berichte* of March 19, 1894, will show that the excuse he makes is wanting in accuracy.

		Freund.	Dunstan and Carr.	
		Calculated.	Found.	Calculated.
Triacetylaconitine		$C_{10}H_{53}NO_{14}$.		$C_{39}H_{51}NO_{15}$.
	C	62·25	60·42	60·54
	H	6 87	6·82	6·59
Diacetylaconitine		$C_{38}H_{51}NO_{13}$.		$C_{37}H_{49}NO_{14}$.
	C	62·55	60·98	60·74
	H	6·99	7·06	6·70
Pyraconitine hydrobromide		$C_{32}H_{43}NO_9HBr$.		$C_{31}H_{41}NO_{10}HBr$.
	C	57·65	55·80	55·69
	H	6·60	6·28	6·28
Aconine		$C_{25}H_{41}NO_9$.		$C_{21}H_{39}NO_{10}$.
	C	60·12	57·31	57·48
	H	8·21	8·02	7·78

Messrs. Freund and Beck have also attempted to show that the isomeric forms of aconitine aurichlorides, as well as aurichlorbenzaconine, described by one of us and Mr. H. A. D. Jowett (Trans., 1894), do not exist, but it has been shown (Proc., February 18, 1895), by a re-examination of these compounds, that our original observations are correct.

Research Laboratory,
Pharmaceutical Society,
London.

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* It will be evident that our new formula for benzaconine, $C_{31}H_{45}NO_{11}$, which Herr Freund asserts is based solely on the analysis of the aurichlor-derivative (the existence of which, by the way, he denies), rests chiefly on the demonstration that exactly one molecular proportion of acetic acid accompanies its production from aconitine.

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		Freund.	Dunstan and Carr.	
		Calculated.	Found.	Calculated.
Triacetylaconitine		$C_{40}H_{53}NO_{14}$.		$C_{39}H_{51}NO_{13}$.
	C	62·25	60·42	60·54
	H	6·87	6·82	6·59
Diacetylaconitine		$C_{38}H_{51}NO_{13}$.		$C_{37}H_{49}NO_{14}$.
	C	62·55	60·98	60·74
	H	6·99	7·06	6·70
Pyraconitine hydrobromide		$C_{32}H_{43}NO_9HBr$.		$C_{31}H_{11}NO_{10}HBr$.
	C	57·65	55·80	55·69
	H	6·60	6·28	6·28
Aconine		$C_{25}H_{41}NO_9$.		$C_{34}H_{39}NO_{10}$.
	C	60·12	57·31	57·48
	H	8·21	8·02	7·78

Messrs. Freund and Beck have also attempted to show that the isomeric forms of aconitine aurichlorides, as well as aurichlorbenzaconine, described by one of us and Mr. H. A. D. Jowett (Trans., 1894), do not exist, but it has been shown (Proc., February 18, 1895), by a re-examination of these compounds, that our original observations are correct.

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MARIGNAC MEMORIAL LECTURE.*

L.—*The Life-Work of Marignac.*

By P. T. CLEVE, Professor of Chemistry in the University of Upsala.

JEAN CHARLES GALISSARD DE MARIGNAC, who was elected a Foreign Fellow of the Chemical Society on the 19th June, 1862, was descended rom Pierre Galissard, Seigneur de Marignac in Languedoc, whose son of the same name was made a citizen of Geneva in 1733. The subject of this memoir was born on April 24th, 1817, at Geneva, where his father, Jacob de Marignac, was a judge and *Conseiller d'Etat*. His mother was the sister of Elie le Royer, whose well-known pharmacy occupied a portion of the house in which the Marignacs resided. This pharmacy is noteworthy in the history of science as the place where Dumas obtained his first instruction in practical chemistry. Le Royer enjoyed a considerable reputation as a chemist and physiologist, and his house in the Rues-Basses was the meeting place of Prevost, De Candolle, and other men of science who were settled in, or who visited, Geneva at that period. These circumstances had, no doubt, their influence in developing the young Marignac's inclination towards natural science, and his life-long friendship with the great French chemist, whom we had also the honour to number among our Foreign Members, dates from this time. At the age of 16, Marignac went to Paris as a student at the *Ecole Polytechnique*, from which he passed—1837 to 1839—to the *Ecole des Mines*. The greater part of the following year was spent in travel in Scandinavia, Denmark, and Germany, the young "élève-ingénieur des mines" being charged with the preparation of reports upon the machinery employed in these countries. The only published outcome of these travels is a description of Henschel's blowing engine in use at the foundry of Veckerhagen, which appears in the *Annales des Mines* for 1824. The notes and drawings which he made during his travels are still preserved, and his biographer, Professor Ador, upon whose charming sketch the present biographical notice is largely based, finds in a note relating to Brussels an indication of that love of solitude and retirement which characterised Marignac through life, in the remark: "Les boulevards qui conduisent au Jardin Botanique sont encore une plus jolie promenade que le parc, car on n'y rencontre personne."

At that epoch, Liebig's laboratory in Giessen was the Mecca towards which nearly every young aspirant for chemical fame directed his steps, and thither Marignac repaired during the winter of 1840, to occupy himself with the study of some derivatives of naphthalene and of phthalic acid; this was his first and last essay in organic chemistry. Prout's hypothesis became to him, as it did to Stas, the primary impulse of almost all his subsequent work; its influence indeed can be detected in nearly all his memoirs in spite of their range and diversity of subject.

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* Chemical Society's Memorial Lectures. No. IV.

Marignac left Germany to take up a post in succession to Malaguti in the famous porcelain manufactory at Sèvres, then under the direction of Alexandre Brongniart, the father-in-law of Dumas, to whose influence the young Genevese chemist doubtless owed his preferment. Although the prospects of the position were promising, Marignac's tastes predisposed him towards an academic career, and in less than half a year he returned to his native town to take up the Professorship of Chemistry in the Academy. "La paie offerte," says Ador, "était modeste, très modeste, la position modeste aussi." To this Chair he added that of Mineralogy in 1845, and he continued to occupy both up to 1878, when the condition of his health compelled him to resign. The laboratory in which he so zealously laboured for upwards of 30 years, and which was the birthplace of his most important investigations, is described as a damp and gloomy cellar, more like the den of an alchemist than the workroom of a modern chemist. Here he worked alone and without assistance. When, in 1873, the Academy grew into the University, Marignac came into possession of the fine laboratory of which Geneva now boasts; and much of his time was occupied in its construction and equipment. He remained here only five years, and on his resignation arranged for himself, on the upper floor of his house in the Rue Senebier, a laboratory, the installation of which was of the simplest nature, quite in harmony with the rare modesty which characterised its owner. He continued to work here until about the year 1884, when his growing infirmity forced him to renounce all scientific investigation. After ten weary years of physical prostration, during much of which he was able to move only from his bed to his armchair, but with a mind active and clear to the last, he was released by death on the 15th April, 1894.

The probity and exactitude of Marignac's work are known to every chemist. In spite of a love of retirement, which it must be admitted in some ways impaired his usefulness as an university teacher, Marignac could not escape the recognition which was extended to him by almost every learned body in Europe. As Cicero says, "magnum virum tamquam umbra gloria sequitur," proved to be true of Marignac. Most scientific societies counted it an honour to number him among their Fellows, and he received many distinctions, among them the Davy Medal in 1886, and the Order "pour le Mérite," given to him in 1881 by the German Emperor.

Marignac's first important work in inorganic chemistry was made with a view to test Prout's hypothesis. He sought to determine as exactly as possible the atomic weights of chlorine, potassium, and silver, thus repeating the work of Berzelius, who says (*Lehrb.*, 3, 1189) that, although he considered his own determinations were not lacking in accuracy, they were surpassed by those of Marignac, and that none before him had attained such a high degree of precision. The great Swedish chemist wrote to Marignac: "Je regrette de n'avoir point pu prévoir, lors de votre visite à Stockholm que celui que je présentais comme un ingénieur des mines devait sitôt commencer à occuper une place élevée dans la chimie." Afterwards Marignac redetermined the atomic weights of bromine, iodine, nitrogen, and carbon; in fact, stoichiometry occupied him to the last, and in the course of his life he determined the atomic weights of no fewer than 28 elements. These researches led him into almost every branch of inorganic chemistry; among these was that of the rare earths, the tantalum group, the fluoro-salts, the complex acids, &c., and in all he made discoveries of the highest significance.

Marignac's work on the rare earths is undoubtedly the most important in this particular department of chemistry. His first investigations were made as early as 1840, when he was barely 23 years of age. Following Mosander, he attacked the cerite earths with the principal object of determining the atomic weights of the elements. The results were published in 1848–49. In 1853, followed a research on didymium. After an interval of more than 20 years, he again returned to the subject of the rare earths—this time to the metals of the yttria group. In 1878, he succeeded in separating ytterbia out of what up to that time was regarded as pure erbia, and it was in examining his fractionations from erbia that Soret found the absorption bands of the metal X, now known to be holmium. In 1880, Marignac extended his researches to the samarskite earths, and succeeded in isolating two new oxides provisionally designated as $Y\alpha$ and $Y\beta$. These are now respectively known as gadolinia and samaria.

A rapid survey of the history of the rare earths will serve to more clearly define Marignac's relations to the development of this branch of chemistry.

In 1794, the Finnish chemist, Gadolin, discovered a new earth or oxide in a black mineral found at Ytterby, near Stockholm. This substance he called yttria. In 1803, another Scandinavian mineral, also known in the past century as "the heavy stone from Bastnäs," and now called cerite, was examined in Sweden by Berzelius and Hisinger, and in Germany by Klaproth. It was found to contain a new oxide, which the Swedish chemists named ceria, after the newly-discovered planet Ceres: Klaproth termed it *ochroiterde*, on account of its yellow colour. Mosander, in 1839, showed that this earth contained another oxide, lanthana, which he subsequently, in 1842, resolved into two distinct oxides, one giving colourless salts, to which he reserved the name lanthana, the other giving pink salts, which he called didymia. At about the same time, Scherer observed that yttria becomes yellow if strongly heated in an open vessel, whereas it is white if heated in a closed crucible, from which he inferred that yttria, like the ceria of Berzelius, was probably a mixture. In the following year, 1843, Mosander proved that by the partial precipitation of yttria salts with ammonia and acid potassium oxalate, the so-called yttria could be resolved into three earths, one of which was white, and gave colourless salts, and for which the name yttria was reserved, the second giving rose-coloured salts, to which the name terbia was given, whilst the third, known as erbia, afforded colourless salts and a deep yellow peroxide. The yttria earths were re-examined in 1860 by Berlin, who, for the first time, employed the method of the partial decomposition of the anhydrous nitrates by fusion. He could only detect two earths in the yttria of Gadolin, namely, the yttria of Mosander, giving white salts, and an oxide, furnishing rose-coloured salts, to which he restricted the name erbia. Hence, according to Berlin, terbia had no existence. All subsequent workers followed Berlin in designating the rose-coloured earth as erbia.

Shortly after the discovery of the spectroscope, Gladstone, in 1858, observed the beautiful absorption spectrum of didymia, and Bahr, in 1862, detected that of erbia. Delafontaine extended the application of the spectroscope in the investigation of the rare earths, and demonstrated the existence in Gadolin's yttria of Mosander's third earth giving a yellow peroxide. Inasmuch, however, as the term erbia had now come to be applied to the rose-coloured oxide, Delafontaine, in resuscitating Mosander's name of terbia, applied it to that earth which had been originally called erbia. In 1866 appeared the work by Bahr and Bunsen, who used Berlin's method, but with the modification that the anhydrous nitrates were so heated that they furnished a residue which was still soluble in boiling water, so that, on cooling, basic nitrates crystallised out. In this manner they succeeded, like Berlin, in resolving Gadolin's yttria into the true or white yttria and rose-coloured erbia, and they further determined the atomic weights on the assumption that these oxides had the general formula RO. The same formula was also applied to the cerite oxides.

In 1871, Mendeléeff published his celebrated paper on the Periodic Law. In discussing the position of these elements in his system, it was necessary to change the formulæ, hitherto considered beyond doubt, of their oxides. For yttria, didymia, and the monoxide of cerium, he proposed the formula R_2O_3; and lanthana he considered to be a dioxide, RO_2. At that time, few facts were known to justify such a change, the compounds of the rare earth metals having been but slightly investigated. The examination of the composition of the yttrium and erbium compounds was the principal object of the researches of Cleve and Höglund, who, in 1873, repeated the work of Bahr and Bunsen. This work was followed, in 1874, by Cleve's new researches on yttria, erbia, didymia, and lanthana, and in 1875 by that of Jolin on the compounds of cerium. The composition of the salts demonstrated the correctness of the predictions of the Russian chemist, with the exception of that relating to lanthana, which was shown to be a sesquioxide. When Hillebrand and Norton in 1875 isolated the metals, their specific heats were found to be in accord with the new atomic weights, and hence with the triadicity of the elements.

In 1878, the chemistry of the rare earths entered upon a new phase; the mineral samarskite, found in large quantities in North America, became now the raw material for preparing them. Whilst it contains much less erbia than gadolinite, it furnishes considerably larger quantities of the yellow earth terbia, as recognised by Delafontaine, from the sparing solubility of its formate. In this mineral, Delafontaine inferred the existence of a new earth, which he named philippia, the formate of which was more soluble in water than the terbium salt. Its salts, which are colourless, are characterised by the absorption band *l* 450. Roscoe (*Chem. Soc. J.*, 1882, 277) subsequently proved that Delafontaine's philippia was a mixture of terbia and yttria. In reality, however, the absorption band belongs to an element now known as dysprosium. A second new metal, decipium, was found in samarskite by Delafontaine (*C. R.*, 87, 632), who at that time characterised it by the absorption bands *l* 416 and *l* 478. Moreover the didymia prepared from samarskite was believed to contain unknown elements. It was subsequently found that the absorption bands *l* 416 and *l* 478 belonged to the element now called samarium. Hence samarium would have been more properly called decipium, had not Delafontaine, in 1881, declared that his decipia of 1878 could be resolved into an oxide without absorption spectrum, for which he retained the name decipia, and into a second with absorption bands for which he adopted the name samaria, given by Lecoq de Boisbaudran. At about this period, Lawrence Smith announced the existence in samarskite of a new metal, which he called mosandrum. Marignac (*C. R.*, 87, 281) and Delafontaine (*C R.*, 87, 600) independently proved that Smith's mosandrum was identical with terbium. Subsequently, Lecoq de Boisbaudran (*C. R.*, 102, 647) showed that mosandria was a mixture of terbia and gadolinia.

Marignac sought to prepare terbia from gadolinite, and succeeded in obtaining an oxide of a deep orange colour, giving colourless salts without absorption spectrum (*Bibl. uni. Arch. sci. ph. nat.*, 61, 283). The atomic weight of the element was found to be 148·5 (Te_2O_3), and much lower, therefore, than the atomic weight, 163·1, as determined in 1886, by Lecoq de Boisbaudran. In examining the erbia from gadolinite, Marignac in 1878 made the unexpected discovery that this earth contained a new oxide, which gives colourless salts without absorption bands (*loc. cit.*, 64, 97). He called the metal of this oxide ytterbium, and assigned to it the atomic weight of 172·5. In the erbia fractions obtained by Marignac, Soret (*C. R.*, 86, 1062) found absorption bands, which could not be attributed to erbium. He called the oxide producing these bands X. In the following year, 1879, Nilson repeated Marignac's work on ytterbium, and found its atomic weight half a unit higher, or 173; he also examined some of its compounds. Lecoq de Boisbaudran and Thalén described its spark spectra. The correctness of Marignac's work was thus substantiated. Nilson, however, found that ytterbia was accompanied by another earth having a lower molecular weight; with the aid of the spectroscopic researches of Thalén he succeeded in proving its individuality, and called the new element scandium. Cleve also examined Mosander's erbia, and found, with Thalén's aid, that the absorption bands hitherto assigned to erbia belonged to three different oxides, one of which, called holmia, was identical with Soret's X, the other, hitherto undetected, between erbia and ytterbia, was called thulia. Cleve also succeeded in extracting Nilson's scandia from gadolinite and from yttrotantalite, and proved that the element scandium corresponded with Mendeléeff's hypothetical *ekaboron*, a conclusion also verified in the following year, 1880, by Nilson.

Neither holmia nor thulia have hitherto been obtained free from the accompanying earths. In 1886, Lecoq de Boisbaudran found that holmia was a mixture of two earths, the true holmia and dysprosium (*C. R.*, 102, 1003), characterised by several bands. Crookes, however, found that only one of these, *l* 451·5, belonged to dysprosia.

At about this time, Marignac turned his attention to the samarskite earths (*Bibl. uni. Arch. sc. ph. nat.*, 1880, 413). By fractionation of the double potassium sulphate salts, he isolated in an almost pure state two oxides, Yα and Yβ; the former was white, and gave colourless salts without absorption bands, the latter gave yellow salts, distinguished by the spectrum of samarium. In the year 1886

(*C. R.*, **102**, 902), the metal in Yα was called gadolinium. It is without doubt a perfectly definite element, although, according to Lecoq de Boisbaudran, Marignac's oxide probably contained about 10 per cent. of foreign oxides (*C. R.*, **108**, 165). Its spark spectrum was examined by Lecoq de Boisbaudran (*C. R.*, **111**, 472). With a sample prepared as pure as possible by Cleve, no emission lines in the spark spectrum could be obtained by Thalén, nor was Bettendorff more successful. The atomic weight of gadolinium was found by Marignac to be 156·75; by Lecoq de Boisbaudran, 155·9; by Cleve, 155 (*C. R.*, **111**, 409); by Bettendorff, 156·33.

The identity of Yβ with the samarium of Lecoq de Boisbaudran, the original decipium of Delafontaine, cannot be doubted. Its individuality has, however, been questioned by Lecoq de Boisbaudran and Demarçay (*C. R.*, 1886, **111**, 1551). Recently (1893) Demarçay has declared that no facts proving the complex nature of samarium have been established (*C. R.*, **117**, 163); Bettendorff has also arrived at the same conclusion (*Annalen*, **256**, 159; **263**, 164). The atomic weight of samarium was found by Marignac to be 149·4; by Brauner, to be 150; by Cleve, as 150·02; by Bettendorff, 150·09.

In the year 1883, Crookes (*Roy. Soc. Proc.*, **35**, 76) made the important discovery that the basic sulphates of certain of the rare earths become phosphorescent when exposed in a vacuum tube to the electric discharge, and that the light so emitted affords characteristic spectra. Soon afterwards (1884) Lecoq de Boisbaudran (*C. R.*, **100**, 1437) discovered another method of obtaining phosphorescent spectra. If the positive pole be immersed in a solution, and the negative pole be brought just above its surface, the light which is emitted gives an inversion spectrum nearly related to that of Crookes. In some cases these spectra are extremely delicate. They are, however, greatly influenced by foreign substances, and in the case of the inversion spectrum of Lecoq de Boisbaudran the character of the spectrum depends upon whether the spark issues at the centre or at the margin of the solution. Moreover, the brilliancy of the bands is not related to the quantity of the active substance present; a mixture of a small quantity with an inert substance may produce a more brilliant spectrum than the pure substance.

Crookes subjected (impure) yttria to an extensive series of fractionations, and found that the bands of the original spectrum became distributed among the different fractions. He considered that yttria was thus split up into a number of components, or, as he termed them, "*meta-elements*," and, on the basis of this observation, he advanced his theory of the "genesis of the elements" (*Chem. Soc. J.*, 1889, 250). The main conclusion was vigorously combated by Lecoq de Boisbaudran, who assigned some of the bands to elements in no wise related to yttria, *Zα* and *Zβ*, of which the former follows holmium, and the latter may be identical with terbium (*C. R.*, **102**, 1536; **103**, 627; *Bull. Soc. Chim.*, 3 (3rd ser.) 53). Perfectly pure yttria gives no phosphorescent spectrum.

It has been pointed out that from the didymia of Mosander Delafontaine extracted samarium. In the year 1885, another element, praseodymium, was separated from didymia by Auer von Welsbach (*Monatsh.*, **6**, 477). This substance is characterised by the green colour of its salts, by its dark brown peroxide, and by its absorption-emission spectrum; its atomic weight is 143·6. It is probable that didymia will still furnish new elements. Its spectrum contains a band, *l* 475, that cannot belong to didymia (Crookes, *C. R.*, 1886, **102**, 1551; Demarçay, *C. R.*, **104**, 580). Another band, *l* 462, according to Demarçay, probably belongs to the same element as that furnishing *l* 475, but Crookes believes it to belong to the samarium series. In the year 1886, Crookes stated that it was possible to eliminate band after band from the original didymium spectrum, so that only the band *l* 443 remained (*Roy. Soc. Proc.*, **40**, 563). Krüss and Nilson (*Ber.*, **20**, 2134, 3067; **21**, 585, 2019), and Kiesewetter and Krüss (*Ber.*, **21**, 2310), on examining the absorption spectra of earths extracted from various minerals, arrived in 1887 at a somewhat similar conclusion, not only as regards didymia, but also as regards all other earths with absorption spectra. Didymia, freed from samaria and praseo-dymia, is said, for example, to contain no fewer than nine elements. C. M. Thompson (*Chem. News*, **64**, 167; *Ber.*, 1891, *Rep.*, p. 975), however, finds that the absorption spectrum of didymium, extracted from various minerals, does not show any difference of importance. With respect to the conclusion of Krüss and Nilson, it must be remembered that the observations were made upon materials containing several oxides giving absorption bands, and it may happen that the intensity of certain bands of a particular element may be increased by the superposition of bands belonging to other elements, (Schottländer, *Ber.*, **25**, 598).

This short survey of the chemistry of the rare earths may be summarised, so far as regards the more important results, as follows:

A. ELEMENTS OF THE YTTRIUM-CERIUM GROUPS PERFECTLY CHARACTERISED.

Scandium.—Atomic weight 44; oxide white; salts colourless without absorption spectrum; spark spectrum rich in lines.

Yttrium.—Atomic weight 88·9 (O = 15·963) or 89·02 (O = 16); oxide white; salts colourless without absorption spectrum; spark spectrum rich in lines.

Lanthanum.—Atomic weight 138·02 (O = 15·963); oxide white; salts colourless without absorption spectrum; emission spectrum rich in lines.

Cerium.—Atomic weight 139·87 or 140·22; oxides: Ce_2O_3, CeO_2, CeO_3; salts of Ce_2O_3 colourless, without absorption spectrum; salts of CeO_2 orange-coloured.

Praseodymium.—Atomic weight 143·6; oxide greenish-white; salts green with absorption spectrum; spark spectrum rich in lines; peroxide, Pr_4O_7, dark brown.

Samarium.—Atomic weight 150; oxide white; salts yellow with absorption bands; spark spectrum rich in lines.

Gadolinium.—Atomic weight 156; oxide white; salts colourless without absorption bands; no spark spectrum (Thalén, Bettendorff); characteristic spark spectrum (Lecoq de Boisbaudran).*

Erbium.—Atomic weight 166; oxide rose-coloured; salts rose-coloured with absorption bands; spark spectrum with few and not brilliant lines (Thalén).†

Ytterbium.—Atomic weight 173; oxide white; salts colourless without absorption spectrum; spark spectrum rich in lines.

B. ELEMENTS OF THE YTTRIUM-CERIUM GROUPS NOT YET THOROUGHLY CHARACTERISED.

Didymium (neodymium).—Atomic weight 140·8; individuality doubted.

Terbium.—Atomic weight 163·1 (Lecoq de Boisbaudran, 1886); salts colourless without absorption spectrum; peroxide brownish-yellow.

Dysprosium.—Absorption spectrum, according to Lecoq de Boisbaudran, 1886, contains the following bands:—*l* 451·5, 475, 456·5, 427·5, and 804(?); Crookes gives *l* 451·5, but excludes the others (*Roy. Soc. Proc.*, **40**, 502).

Holmium.—Salts give absorption bands *l* 640·4, 536·3 (Lecoq de Boisbaudran).

Thulium.—Salts give absorption bands *l* 684, 464·5.

Zα (Lecoq de Boisbaudran, 1885) follows holmia reversion bands *l* 573, 476·12; identical with Crookes' Gδ (*C. R.*, 1886, **102**, 899).

Zβ (Lecoq de Boisbaudran, 1885) reversion bands *l* 620·5, 585·75 (double), 543·2, 487 (*C. R.*, *loc. cit.*); apparently identical with Crookes' Gζ and probably terbia.

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* The difference depends on the methods used by the experimenters.

† According to Kruss, erbia may be complex. The conclusion cannot, however, as yet be considered as proved.

Zγ (Lecoq de Boisbaudran, 1886. *C. R.*, 102, 153) follows holmia and Zα characterised by its spark spectrum.

Zϵ (Lecoq de Boisbaudran, 1892) follows samarium; spark spectrum lines *l* 459·3, 466·2, 462·7 (*C. R.*, **119**, 575).

Zζ (Lecoq de Boisbaudran, 1892) follows samarium reversion bands *l* 611·2 sharply defined, fading away at *l* 622 (*C. R.*, **119**, 575).

Gα (Crookes, 1886) vacuum band *l* 482.

Gβ (Crookes) vacuum band *l* 550, 541; either terbia or Lecoq's Zβ (*C. R.*, **103**, 114).

Gγ (Crookes) vacuum band *l* 568, 563.

Gδ (Crookes) vacuum band *l* 574; probably identical with Lecoq's Zα.

Gϵ (Crookes) vacuum band *l* 597.

Gζ (Crookes) vacuum band *l* 619; probably identical with Lecoq's Zβ.

Gη (Crookes) vacuum band *l* 647.

Sδ (Crookes) vacuum band *l* 609; gadolinium according to Bettendorff (*C. R.*, **102**, 1464; *Annalen*, **270**, 382).

Sγ (Crookes) vacuum bands *l* 456.

Unknown element with the absorption bands *l* 550 and *l* 493 in the spectrum of impure erbium; does not occur in thulium, erbium, holmium, and dysprosium (Crookes, *Roy. Soc. Proc.*, 1886, **40**, 502).

Unknown element with the absorption band *l* 475 in the didymium spectrum (Crookes, *C. R.*, **102**, 1551; Demarçay, *C. R.*, 1886, **102**, 1552).

Unknown element with the absorption band *l* 462 in the old didymium spectrum; according to Demarçay (*C. R.*, **104**, 580), it is the same element as that which gives rise to *l* 475. According to Crookes it belongs to the samarium series.

Unknown element with the absorption band *l* 434 in the old didymium spectrum (Demarçay, *C. R.*, 1886, **102**, 1552).

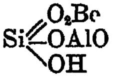
In 1801, Hatchett investigated a black mineral found in North America, subsequently known as columbite, and discovered in it a new element which he called columbium. In 1804, Ekeberg, when examining yttrotantalite from Ytterby and tantalite from Finland, isolated a new metallic substance which he called tantalum. Shortly afterwards Wollaston declared that columbium and tantalum were identical. Berzelius in 1815 studied tantalic acid which he at first formulated as TaO_3, but subsequently as Ta_2O_3.

In 1840, Wöhler examined the acid oxides in pyrochlore, and made known the characteristic blue colour which they give with hydrochloric acid and zinc, and he also discovered the white volatile oxychloride. For nearly 20 years, Heinrich Rose in Berlin, and Rudolph Herman in Moscow, occupied themselves with the study of the metals of the tantalum group. I can only very briefly summarise the results of their prolonged investigations. The main conclusion of Rose's work was to show that these minerals contained the elements tantalum, giving the oxide TaO_2, and niobium, yielding the oxides NbO_2 (niobic acid, formerly known as pelopic acid) and Nb_2O_3 (hyponiobic acid, formerly called niobic acid). The chloride corresponding with NbO_2 was yellow; the hyponiobic chloride was the white substance first observed by Wöhler, and now known to be an oxychloride. Herman in 1846 believed there existed another metal, *ilmenium*, but Rose proved that the so-called ilmenic acid was a mixture of oxides of niobium. To add to the chaos, Franz von Kobell in 1860 announced the discovery of still another acid—*dianic* acid—belonging to this group. About the year 1865, however, the subject became clear through the independent researches of Marignac and Blomstrand. Marignac examined the fluoro-salts, and Blomstrand the chlorides. Both found that there existed only two metals in this group, namely, niobium and tantalum, and that the white hyponiobic chloride was an oxychloride. Blomstrand formulated niobic acid as NbO_2, and the white oxychloride $Nb_4O_3Cl_{10}$. Marignac proved the isomorphism of the hyponiobic fluoro-salts with the fluoro-salts of tin and tungsten. He found that niobium oxyfluoride was $NbOF_3$, and that in consequence hyponiobic acid became Nb_2O_5, and that the niobic acid of Rose had no existence. These conclusions were verified by the determination of the vapour density of niobic oxychloride by Troost and Hautefeuille. It was found to correspond with $NbOCl_3$ and not with Nb_2Cl_3. Rose's chloride of niobium, $NbCl_4$, was in reality $NbCl_5$. Marignac further established that the formula of tantalic acid was Ta_2O_5.

In 1858, Marignac pointed out that the fluorstannates and fluorsilicates were isomorphous. This fact settled the long discussed question of the formula of silicic acid. Prior to that time, silicic acid was usually written SiO_3, but the formula was now definitely decided to be SiO_2. The change was not only of great importance to chemistry, but produced a revolution in mineralogy. It marks, indeed, a new epoch in the history of that science.

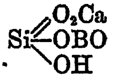
This research was followed in 1860 by a similar examination of the fluoro-salts of zirconium, from which it became evident that the oxide of that element must be ZrO_2 instead of Zr_2O_3, as hitherto supposed. Subsequently Marignac examined the fluoro-salts of boron, tungsten, antimony, and arsenic. The research on the fluoro-salts of tungsten led to the important discovery of silicotungstic acid, which first directed the attention of chemists to the existence of the important class of acids known as the complex mineral acids.

In examining the compounds of vanadium, Berzelius discovered a remarkable silico-vanadium-phosphoric acid. He was also the first to note the yellow precipitate which acidified ammonium molybdate gives with phosphoric acid, and which was first analysed in 1849 by Svanberg and Struve. Marignac's discovery of silico-tungstic acid again directed the attention of chemists to this class of compounds. A considerable number of such acids have now been made known by the researches of Blomstrand, Friedheim, Wolcott Gibbs, Kehrman, Péchard, Rosenheim, Scheibler, and others; but it is still very difficult to give a comprehensive theory of their constitution. It may be assumed that the complex acids contain two different negative radicles united by oxygen, and that this combining atom of oxygen is the residue of a hydroxyl group corresponding with the hydroxyl of the alcohols. To this class belongs a considerable number of salts formerly considered as double salts, but distinguished by abnormal reactions, as the chromo-oxalates, platino-oxalates, and the chromo-sulphates recently investigated by Recoura. This class of complex acids is very large, and it can hardly be doubted that salts of such acids exist in nature. Some natural borosilicates may indeed be considered as salts of complex acids; for instance, tourmaline may be represented as $\mathrm{B}\Big\langle\begin{matrix}(\mathrm{SiO_4R_3})_2\\ \mathrm{O\overset{III}{R}O}\end{matrix}$. The rare Norwegian mineral, cappelenite, may be formulated as $\mathrm{B}\Big\langle\begin{matrix}\mathrm{SiO_4Y}\\ \mathrm{O_2Ba}\end{matrix}$, and the analogous and isomorphous nordenskiöldine as $\mathrm{B}\Big\langle\begin{matrix}\mathrm{SnO_4B}\\ \mathrm{O_4Ca}\end{matrix}$. Boron, aluminium, and yttrium play a similar part in minerals, as may be seen on comparing the following formulæ:



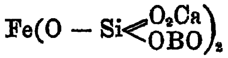
$$\mathrm{Si}\Big\langle\begin{matrix}\mathrm{O_2Be}\\ \mathrm{OAlO}\\ \mathrm{OH}\end{matrix}$$

Euclase



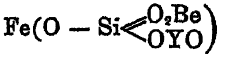
$$\mathrm{Si}\Big\langle\begin{matrix}\mathrm{O_2Ca}\\ \mathrm{OBO}\\ \mathrm{OH}\end{matrix}$$

Datholite.



$$\mathrm{Fe}\left(\mathrm{O}-\mathrm{Si}\Big\langle\begin{matrix}\mathrm{O_2Ca}\\ \mathrm{OBO}\end{matrix}\right)_2$$

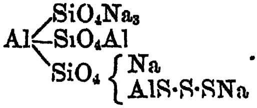
Homilite.



$$\mathrm{Fe}\left(\mathrm{O}-\mathrm{Si}\Big\langle\begin{matrix}\mathrm{O_2Be}\\ \mathrm{OYO}\end{matrix}\right)$$

Gadolinite.

It is then probable that many of the natural aluminous silicates may be salts of alumina-silico-acids. On the basis of the researches of Tschermak, Clarke, and others, we may assume the existence of the acids $\mathrm{Al(SiO_4H_3)_3}$ and $\mathrm{Al(Si_3O_8H_3)_3}$. From the former, we derive an anorthite; from the latter, orthoclase. Salts of these acids are also met with in the groups of the micas and zeolites. The first acid gives rise to such minerals as garnet, nepheline, sodalite, topaz, and andalusite. We may also conceive that ultramarine is derived from the same acid, since, according to the researches of Brogger and Bäckstrom, it may be formulated as



$$\mathrm{Al}\begin{cases}\mathrm{SiO_4Na_3}\\ \mathrm{SiO_4Al}\\ \mathrm{SiO_4}\left\{\begin{array}{l}\mathrm{Na}\\ \mathrm{AlS{\cdot}S{\cdot}SNa}\end{array}\right.\end{cases}$$

A certain number of minerals, as leucite and spodumene, are derived from $\mathrm{Al}\!<\!\begin{smallmatrix}\mathrm{SiO_3}\\ \mathrm{SiO_3R}\end{smallmatrix}$; others, as petalite, from $\mathrm{Al}\!<\!\begin{smallmatrix}\mathrm{Si_3O_7}\\ \mathrm{SiO_3H}\end{smallmatrix}$.

The foregoing examples will serve to show how important the study of the complex acids may become as serving to simplify the formulæ of the silicates, and in so bringing them into natural groups.

The chemistry of minerals had always great interest for Marignac, and he analysed numbers of them during the period from 1840 to 1851; many of these were collected during his travels in the Alps with his distinguished friend DesCloiseaux. His account of the analysis of æschynite is noteworthy by reason of the new analytical methods employed.

Analytical chemistry is, indeed, indebted to Marignac for a number of methods of quantitative analysis. As an example of the care with which these were worked out, I may refer to his paper on the analyses of the borates and fluorborates, in which accurate processes for the determinations of fluorine and boron, confessedly difficult quantitative operations, are given (*Zeitschr. anal. Chem.*, 1, 405).

Geneva is especially associated with the chemistry of ozone, and Marignac had his share in proving its true nature. As far back as 1845, he showed that this substance, contrary to the statements of Williamson and Baumert, was free from hydrogen.

Few of Marignac's papers were published in English, or found their way into our journals through the medium of translations. A noteworthy exception, however, occurs in the case of a paper in the *Philosophical Magazine* for 1846, p. 527, which consists of a somewhat trenchant criticism of the well-known paper by Playfair and Joule on "Atomic Volume and Specific Gravity," read before this Society on May 17, 1845. Marignac contended that Playfair and Joule's statement "that the volume occupied by an equivalent of any salt whatever in solution in water is always an exact multiple of the number representing the atomic volume of water" has no foundation in fact, and that the experimental evidence adduced by its authors was vitiated by the arbitrary manner in which the temperatures of comparison had been selected. Marignac shows that the molecular volume of a salt in solution depends both on the temperature and on the relative proportions of water and salt, and these circumstances cause the volume to vary within considerable limits. So long as these influences are neglected, or so long as we operate in such manner that they do not act in all cases in the same manner, the results obtained cannot be compared with one another. Marignac further contended that Playfair and Joule's law "that the atomic volume of any salt whatever is a multiple of 11, or of a number near to 11, or a multiple of 9 8 (the molecular volume of ice), or, again, the sum of a multiple of 11 or of 9·8," has no valid experimental foundation, and that the apparent concordance between theory and experiment is due to the arbitrary and irrational manner in which the factors 9, 8, or 11 were selected.

Marignac's criticism on Than's paper on "The Anomalous Vapour Density of Sal-ammoniac" (*Bibl. univ. Arch. sc. phys. nat.*, 1865, **22**, 5), and his own communication on "The Latent Heat of Vaporisation of Sal-ammoniac" (*C. R*, 1868, **67**, 877), are interesting as throwing light on the nature of the change which this compound suffers on being heated—a question which has now only an historical interest, but which, 30 years ago, was of the highest importance in regard to Gerhardt's extended application of the hypothesis of Avogadro. Although no final numerical values could be obtained, the numbers which Marignac gives in the latter paper can only be explained on the assumption that the substance, on volatilisation, was almost completely resolved into its proximate constituents. It was found that the quantity of heat required to volatilise sal-ammoniac is almost exactly the same as would be required, according to the experiments of Favre and Silbermann, to decompose it. Any other conclusion would imply that sal-ammoniac possessed a heat of volatilisation absolutely anomalous when compared with that of similar substances, or that scarcely any heat was evolved by the union of its elements, that which is observed at the time of its formation being only the result of its condensation to the solid state. Similar observations by Marignac with sulphuric acid showed that the latent heat of volatilisation of this substance was practically equal to the heat of decomposition, thus substantiating the hypothesis of the decomposition of sulphuric acid by heat advanced by Wanklyn and Robinson as a result of their experiments on the diffusion of its vapour. The desire expressed by Marignac for an accurate method of measuring the heat concerned in reactions which take place at high temperatures, although not actually fulfilled, approaches realisation, and we may well hope that the methods employed by Le Chatelier, Callendar, Griffiths, and others, may find speedy application in this particular department of thermochemistry.

Marignac's most important researches in physical chemistry are, however, concerned with his labours on the nature and process of solution. This work, involving the determination of a number of thermal magnitudes, was done with the same skill and care which he bestowed upon his stoichiometric work, and it furnishes us with a series of numerical data which are of the highest importance in regard to the general theory of the subject.

The publication of Thomsen's thermochemical researches led Marignac to communicate the results of a number of observations on the thermal effects produced by the dilution of saline solutions. He had, in fact, prior to the publication of Thomsen's work, undertaken an investigation on much the same lines, which, however, he was deterred from prosecuting, owing to the impossibility of eliminating the effects produced by the intervention of the solvent employed, and which, he maintains, had been insufficiently appreciated in researches of this character.

Marignac ascertained that for many salts the effect of dilution could be neglected, provided that solutions were used containing at most one-fortieth part of the salt; in other cases, on the contrary, the effects were perceptible not in lowering the temperature as the dilution increased, but in raising it. Such was the case with sulphuric acid, and with the acid sodium sulphate due to the decomposition of this salt by the water. When solutions of two salts which do not give rise to double decomposition are mixed, the variation in temperature is generally less than that resulting from the mixture of these solutions with water; there is usually an evolution of heat when two salts are incapable of combining with each other, absorption when they can form a double salt, variations which become, however, almost inappreciable in solutions of 1 in 40. Sulphuric acid mixed with alkali sulphates gives rise to a considerable absorption of heat. In diluting a solution containing two salts incapable of decomposing each other, the thermal effect is nearly equal to the algebraic sum of the effects which would follow on taking the salts separately. Marignac, by studying the interaction of acids and salts, proved that the action, chemical or otherwise, varies with the proportion of water in which it takes place. The thermal effect is entirely different according to the dilution; it even changes its sign in the case of sulphuric acid and sodium nitrate. Here, therefore, there is chemical decomposition between the mixed salts, and this decomposition increases with the proportion of water. The same is the case in the double decompositions of neutral salts, which appear to be the more complete the more their solutions are diluted. These phenomena would seem to receive their explanation in our modern theories of solution. We see that the interdependence between the pressure and the stability of a gaseous system, capable of dissociation, has its analogy in a similar interdependence between the osmotic pressure and the particular phase of a changeable system in solution.

In the course of these investigations, Marignac observed the following curious anomaly. Supposing we have to dilute solutions of 1 in 10 so as to make a mixture of two substances in a solution of 1 in 80, we may either mix the two solutions of 1 in 10 directly and then add seven times the volume of water, or else first dilute each solution to 1 in 80 separately, and subsequently mix them. When the two methods were actually employed, it was found that the sum of the thermal effects was not the same. Marignac eventually discovered that the explanation was due to the alteration of the specific heats of the solutions. His method of measuring the specific heat of aqueous solutions consisted in determining the relative weights of water and of liquid under examination, that showed the same change in temperature on the addition of the same quantity of heat—a method which eliminated several external causes of error. Unfortunately, Marignac was anticipated in the prosecution of his work by Thomsen, and only the general results of his experiments were published.

The difference between the specific heat of a solution and the sum of the specific heats of its elements is the proof, and approximately the measure, of the work done by the chemical reaction causing the change of temperature of the liquid. It was established that dilution always produces contraction. When water is mixed with a solution, the coefficient of expansion of the mixture is higher than the mean of the coefficient of the two mixed liquids: it follows from this that the contraction caused by the mixture diminishes in proportion as the mixture is effected at a higher or lower temperature, and we may thence conclude that at a temperature sufficiently high the dilution of solutions will give rise neither to contraction nor to a reduction of specific heat.

In a subsequent memoir (*Bibl. univ. arch.*, 1876, 55, 113), Marignac attempted to determine whether the specific heats of saline solutions are so connected with the nature of the acid and base that they form parallel series, such that the specific heats may be approximately calculated (as may be done in the case of densities) when the separate effect of base and acid has been determined in other salts; or whether the specific heat varies from one salt to another from causes independent of the nature of acid and base. If the latter alternative be established, it becomes necessary to ascertain the relation between the variations in specific heat and some other property of the salts, in particular their tendency to form definite crystalline hydrates. After two years' continuous labour, during which he frequently made as many as a dozen observations a day, he found that the specific heat of saline solutions always increases with the temperature, and in proportion to the degree of concentration of the solutions. This increase is very rapid in the case of certain solutions, *e.g.*, copper sulphate, but the specific heat does not exclusively depend on the nature of the acid and base, and has apparently no relation to the greater or less tendency of salts to combine with water to form definite crystallisable hydrates. It seems rather to be related to the existence of definite but dissociated hydrates, the proportion of which varies with that of the water and with the temperature.

In this connection we may refer to Marignac's work on the solubility of calcium sulphate in water. Having accidentally observed that a solution of this salt contained more of the substance than corresponded with its supposed solubility, he was led to find that its solubility increases from 0° to 32°, attains a maximum between 32° and 41°, and then diminishes. The phenomena of supersaturation of calcium sulphate were identical in kind with those observed in the case of sodium sulphate.

When we have regard to the amount of work which has been bestowed upon it, no field of research in chemical physics has proved less fruitful than that of liquid diffusion. In spite of much laborious investigation, the subject remains very much as Graham left it, and although a great amount of experimental matter has been accumulated, few broad general principles, other than those which our first President made known, have been obtained. Marignac brought all the qualities of patient industry, manipulative skill, and a rigorous sense of accuracy to the elucidation of the problem, especially in regard to the simultaneous diffusion of mixed substances. He attempted to estimate the relative coefficient of diffusion of two salts from measurements of their simultaneous diffusion. But the main outcome of a prolonged investigation was to establish that the mixture of two substances always diminishes the diffusibility of the less diffusible of the two. He found that it was immaterial whether mixtures of equal weights or mixtures of equivalent proportions were operated upon. The degree of concentration of the solution had a variable influence on the relative coefficient of simultaneous diffusion, sometimes increasing with increasing dilution, sometimes remaining unchanged, and sometimes diminishing as the proportion of water to salt is increased. The most important general result is that the rates of diffusion of the acids are related to those of the metals in such manner that the salts of any specified acid always follow in the same order whatever the acid may be, and that all the salts of any metal follow in the same order, independently of the nature of the metal. The following table shows the order of the diffusion coefficients.

Cl, Br, I	H
NO_3	K, NH_4
ClO_3, ClO_4, MnO_4	Ag
F	Na
CrO_4	Ca, Sr, Ba, Pb, Hg.
SO_4	Mn, Mg, Zn
CO_3	Cu
	Al

The analogy which this table manifests to that of the conductivity of salt solutions is highly suggestive in relation to our present conceptions of the true nature of solution (compare Ostwald, *Solutions*, p. 139).

It is significant of his grasp of principles, and of the logical order of his thought, that Marignac, during the memorable discussion that took place before the Académie des Sciences, at Paris, in May and June, 1877, on equivalency and atomic weights, should have taken up a position which is in entire accord with that which we occupy at present. His contention, which at that time brought him into direct conflict with Berthelot, more particularly in regard to the criteria which should guide chemists in the selection of the several possible atomic weights that chemical considerations alone would serve to indicate, expresses the settled conviction of to-day.

Modest, patient, and unassuming, transparent in character, and honest of purpose, with no other conception of his calling than that of pursuing truth for truth's sake, Marignac lived wholly for science, and no man has served her with a purer or more unselfish devotion. If the world of science is the poorer by his loss, it is the richer by his example.

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LI.—*Action of Nitrosyl Chloride on Amides.*

By WILLIAM A. TILDEN, D.Sc., F.R.S., and MARTIN O. FORSTER, Ph.D.

Acetamide, $CH_3{\cdot}CO{\cdot}NH_2$.—When a current of nitrosyl chloride is passed into a solution of acetamide in chloroform at —10°, a precipitate, consisting of acetamide hydrochloride immediately begins to separate. The product from one experiment, when recrystallised from a mixture of benzene and alcohol, melted at 132°, and was found to contain 23·33 per cent. of chlorine; the formula $(C_2H_3O{\cdot}NH_2)_2HCl$ requires 22·97 per cent. of chlorine.

A further action takes place when acetamide, dissolved in excess of liquid nitrosyl chloride, remains in sealed tubes at the ordinary temperature. The amide is completely decomposed, and on allowing the excess of nitrosyl chloride to evaporate, a pale yellow liquid remains, consisting of acetic acid with hydrogen chloride in solution. The reaction probably proceeds in two stages, thus

$$CH_3{\cdot}CO{\cdot}NH_2 + NOCl = CH_3{\cdot}COCl + N_2 + H_2O.$$
$$CH_3{\cdot}COCl + H_2O = CH_3{\cdot}COOH + HCl.$$

This view is confirmed by the similar behaviour of benzamide.

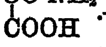
Benzamide, $C_6H_5{\cdot}CO{\cdot}NH_2$.—Benzamide, suspended in cold, well-dried ether, also gave a precipitate of the hydrochloride. When sealed up with liquid nitrosyl chloride, a considerable rise of temperature occurred on removing the tube from the freezing mixture, and the benzamide became dissolved. After allowing the nitrogen to escape, and the excess of liquid to evaporate, a residue was obtained, consisting of benzoic acid saturated with benzoic chloride.

Oxamide, $C_2O_2(NH_2)_2$.—Oxamide undergoes no change when suspended in cold ether and submitted to the action of the gas. Even when heated with liquid nitrosyl chloride at 100°, it remains unaltered.

Oxanilide, or Phenyloxamide, $C_2O_2(NH{\cdot}C_6H_5)_2$.—Oxanilide also undergoes practically no change in contact with the reagent. After being heated with the liquid for three hours at 90°, the residue obtained on evaporation contained a small quantity of chlorine, but consisted chiefly of unaltered oxanilide having the same melting point, namely 245°.

Malonamide, $CH_2(CO{\cdot}NH_2)_2$.—At common temperatures, malonamide is acted on very slowly by the reagent, a substance which behaves as an oxime being formed in small quantity. This is probably nitrosomalonic acid, $C(NOH)(COOH)_2$. It dissolves in alkalis with a yellow coloration, and the aqueous solution becomes red on adding ferric chloride; when treated with ferrous sulphate and a drop of any alkali, a very striking, intensely purple coloration is produced

When malonamide is sealed up with liquid nitrosyl chloride and heated at 100°, complete decomposition occurs, hydrogen chloride and nitrogen being evolved, whilst the residue melts at 132°, and is found to consist of malonic acid with a small quantity of malonic chloride. The behaviour of malonamide, therefore, under these conditions, resembles that of all the other amides, excepting oxamide, the stability of which is remarkable.

Oxamic acid,  $\begin{array}{l}CO{\cdot}NH_2\\ |\\ COOH\end{array}$.—With liquid nitrosyl chloride in the cold no action occurs, but when heated at 100° for about an hour the acid is completely converted into pure oxalic acid.

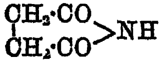
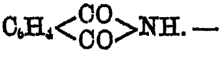
Carbamide, $CO(NH_2)_2$.—When finely powdered urea is allowed to fall in small quantites at a time into liquid nitrosyl chloride, brisk effervescence occurs, accompanied by rise of temperature. The gases when collected over water are found to consist of carbonic anhydride, nitrogen, and nitric oxide, the last-named being manifestly due to the decomposition of the nitrosyl chloride vapour. If the excess of chloride is allowed to evaporate, a very deliquescent yellow solid remains. This is decomposed by water, with evolution of a small quantity of nitrogen; 0·4994 gram gave 1·6 c.c. of moist nitrogen at 14° and 738 mm., this amount corresponding to 0·36 per cent. The substance also contains 37·4 per cent. of chlorine. It appears, therefore, to consist of urea hydrochloride (which contains 36·78 per cent. of chlorine). retaining a small quantity of nitrosyl chloride.

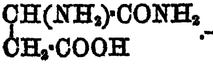
The primary action probably consists in the formation of carbonyl chloride, nitrogen, and water. This view is supported by the corresponding interaction which occurs in the case of urethane.

Urethane, $C_2H_5O\cdot CO\cdot NH_2$.—In contact with liquid nitrosyl chloride at about —15°, effervescence takes place, and the escaping gas contains carbonic anhydride. On allowing the excess of nitrosyl chloride to escape, a yellowish liquid is left, consisting chiefly of ethylic chlorocarbonate, $C_2H_5O\cdot COCl$.

Glycocine, $CH_2(NH_2)\cdot COOH$.—When glycocine is allowed to fall into liquid nitrosyl chloride at temperatures below —10°, no change takes place; if, however, dry glycocine is allowed to remain in contact with liquid nitrosyl chloride for several hours at the ordinary temperature, it dissolves completely and nitrogen is evolved. On allowing the excess of chloride to evaporate, an oil is obtained, which solidifies to a paste of crystals when cooled; this substance is chloracetic acid. It melts at 65°, and yields a barium salt which crystallises from hot water in small, colourless needles, containing 39·9 per cent. of barium. Another preparation, when dried at 70°, contained 22·25 per cent. of chlorine. The formula $(C_2H_2ClO_2)_2Ba + H_2O$ requires 40·05 per cent. of barium and 20·70 per cent. of chlorine; the anhydrous salt contains 21·91 per cent. of chlorine.

Hippuric acid, $CH_2(NH\cdot C_7H_6O)\cdot COOH$.—Hippuric acid is not acted on by nitrosyl chloride, whether in ethereal solution or when sealed up in a tube with the liquid chloride. Even when heated with the chloride for two hours at 90° it remains unchanged; no gas is evolved, and the solid residue obtained on evaporation melts at 188°, and is free from chlorine.

Succinimide,

$\begin{matrix} CH_2\cdot CO \\ | \\ CH_2\cdot CO \end{matrix}\!\!>NH$, *and Phthalimide*,

$C_6H_4\!<\!\begin{matrix} CO \\ CO \end{matrix}\!>\!NH$.—
Succinimide and phthalimide are not acted on by nitrosyl chloride alike when suspended in chloroform, and when heated at 100° with the liquid chloride in a sealed tube. Succinimide passes into solution and crystallises out on cooling, but phthalimide remains undissolved, and undergoes no change, even when heated at 150° with liquid nitrosyl chloride.

Asparagine (*ordinary lævorotatory*),

$\begin{matrix} CH(NH_2)\cdot CONH_2 \\ | \\ CH_2\cdot COOH \end{matrix}$.—With liquid nitrosyl chloride in a sealed tube, there is no visible action at the

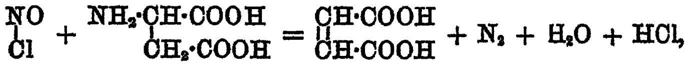
ordinary temperature, but at 40—50° evolution of gas takes place, and a layer of colourless liquid, evidently strong aqueous hydrochloric acid, collects at the bottom of the tube. The crystalline residue melts at about 172°; it is not, therefore, unchanged asparagine.

In order to operate on a larger quantity of material, 50 grams of asparagine were dissolved in hot, strong hydrochloric acid, and submitted to the action of a current of the gas; effervescence set in immediately, and soon a copious, white, crystalline precipitate was formed. When all action had ceased, this was removed and drained, and, after recrystallisation, was easily identified as fumaric acid. On evaporating the mother liquor, a crystalline residue was obtained; this was very soluble in water, from which it crystallised slowly in thick, colourless prisms, melting at about 172°, with evolution of gas. Analysis gave the following numbers, which show that the substance is a chlorosuccinic acid.

	Found.	Calculated for $C_4H_5ClO_4$.
Carbon	31·88	31·50
Hydrogen	3·25	3·28
Chlorine	21·94 and 21·98	23·23

The high melting point of the substance indicates that it is not identical with the acid obtained by Anschütz and Bennert by heating fumaric acid with hydrogen chloride dissolved in glacial acetic acid (*Ber.*, 1882, **15**, 642).

When the solution into which the nitrosyl chloride is passed is kept cool, a considerable quantity of ammonium chloride is formed. Probably, therefore, asparagine is first hydrolysed into aspartic acid, this substance being then converted into chlorosuccinic acid by the exchange of the amido-group for chlorine. The production of fumaric acid is also probably due to the direct action of nitrosyl chloride,

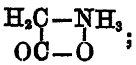


$$\begin{matrix} NO \\ | \\ Cl \end{matrix} + \begin{matrix} NH_2\cdot CH\cdot COOH \\ | \\ CH_2\cdot COOH \end{matrix} = \begin{matrix} CH\cdot COOH \\ \| \\ CH\cdot COOH \end{matrix} + N_2 + H_2O + HCl,$$

and not to the splitting up of preformed chlorosuccinic acid.

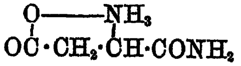
From the experiments described, it appears that the primary action of nitrosyl chloride on amides consists in the exchange of NH_2 for Cl. This agrees with the observation of Mr. Titherley regarding the action of the same substance on potassamide, as expressed by the equation $KNH_2 + NOCl = KCl + N_2 + H_2O$ (Trans., 1894, **65**, 521).

The cases of glycocine and asparagine possess an especial interest in view of the recent proposal by Professor Sakurai to revive the closed chain formulæ for these compounds (Erlenmeyer and Sigel, *Annalen*, 1875, **176**, 349). Glycocine he would represent as



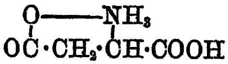
$$\begin{array}{l} H_2C-NH_3 \\ \;\,|\quad\;\;| \\ OC-O \end{array};$$

asparagine and aspartic acid as



$$\begin{array}{l} O\text{———}NH_3 \\ |\qquad\quad| \\ OC\cdot CH_2\cdot CH\cdot CONH_2 \end{array}$$

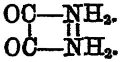
and

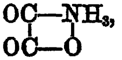


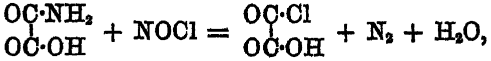
$$\begin{array}{l} O\text{———}NH_3 \\ |\qquad\quad| \\ OC\cdot CH_2\cdot CH\cdot COOH \end{array}$$

respectively (Proc., 1894, 93). As glycocine, however, reacts with nitrosyl chloride in the same manner as other compounds which undoubtedly are amides, it would appear to have a similar constitution. Moreover it would be difficult to explain by Sakurai's formula the production of chloracetic acid from glycocine by this agent, for we should expect to see the complete removal of the NH_3-group by NOCl, with formation of N_2, H_2O, and HCl, and certainly it would be in the highest degree improbable that, in the presence of such a reagent, hydrogen should return to the oxygen to reproduce the hydroxyl necessary to form an acid.

As to asparagine, it might be argued that an additive-compound is formed, but this hypothesis will not account for the replacement of NH_2 by Cl in the production of chlorosuccinic acid.

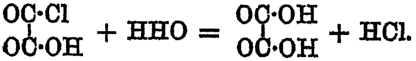
The only case observed in which an undoubted amide is not attacked by nitrosyl chloride is oxamide. It is possible that this may be accounted for by the hypothesis that in this compound the nitrogen atoms are linked together thus,  $\begin{array}{l} OC-NH_2. \\ \;|\qquad\| \\ OC-NH_2. \end{array}$

The formula for oxamic acid might be  $\begin{array}{l} OC-NH_3, \\ \;|\qquad| \\ OC-O \end{array}$ but this representation is inconsistent with the fact that oxamic acid is entirely converted into oxalic acid by nitrosyl chloride, doubtless through the intermediate formation of the chloride, which reacts with the water simultaneously produced:



$$\begin{array}{l} OC\cdot NH_2 \\ \;| \\ OC\cdot OH \end{array} + NOCl = \begin{array}{l} OC\cdot Cl \\ \;| \\ OC\cdot OH \end{array} + N_2 + H_2O,$$

and



$$\begin{array}{l} OC\cdot Cl \\ \;| \\ OC\cdot OH \end{array} + HHO = \begin{array}{l} OC\cdot OH \\ \;| \\ OC\cdot OH \end{array} + HCl.$$

LII.—*Action of Nitrosyl Chloride on Asparagine and Aspartic Acid. Formation of Lævorotatory Chlorosuccinic Acid.*

By WILLIAM A. TILDEN, D.Sc., F.R.S., and B. M. C. MARSHALL, A.R.C.S.

Two chlorosuccinic acids are known, the one obtained by the action of hydrogen chloride on fumaric acid is optically inactive and melts at 152° (Anschutz and Bennert, *Ber.*, 1882, **15**, 642), the other formed by the action of phosphoric chloride on ordinary malic acid is dextrorotatory and melts at 174° (Walden, *Ber.*, 1892, **26**, 215).

The action of nitrosyl chloride on asparagine having been found to result in the production of a chlorosuccinic acid with melting point above 170° (preceding paper), it seemed desirable to examine rather more in detail the circumstances of its formation and its properties. A preliminary examination showed that the acid in aqueous solution was lævorotatory.

The asparagine used in the experiments had a specific rotatory power when dissolved in water $[\alpha]_D = -4{\cdot}80^\circ$. It was dissolved in about three times its weight of ordinary concentrated hydrochloric acid, and the gaseous nitrosyl chloride passed into the solution until the liquid was permanently yellow, showing excess. The proportion of hydrochloric acid used did not appear to affect the result, but the temperature at which the experiment was conducted had a decided influence. The products formed are fumaric acid, chlorosuccinic acid, and ammonium chloride. The production of ammonium salt proves that the amido-group of the asparagine is hydrolysed by the action of the acid, and that the substance actually submitted to the action of the nitrosyl chloride is chiefly aspartic acid. As ammonium chloride at temperatures up to 30° is almost wholly unaffected by nitrosyl chloride, the salt accumulates in the solution when the experiment is carried on at low temperatures, whilst it is for the most part destroyed when the solution is heated. Theoretically, 100 grams of asparagine would give 78 grams of fumaric acid or 101 grams of monochlorosuccinic acid.

Four experiments gave the following products calculated for 100 grams of asparagine.

I. Solution kept cool; 28 grams of fumaric acid, much NH_4Cl and a few grams only of chlorosuccinic acid.

II. Temperature about 60°; 20 grams of fumaric with 40 grams of chlorosuccinic acid.

III. Boiling; 44 grams of fumaric with 9 grams of chlorosuccinic acid.

IV. Solution kept cool at first, then heated to boiling after excess of nitrosyl chloride had been introduced; 4 grams of fumaric acid with 66 grams of chlorosuccinic acid.

In all the experiments, there appears to be considerable destruction of material probably owing to the oxidising action of the reagent.

The solution was in each case evaporated on a water bath, and the dry residue treated with the least possible quantity of cold water, in which fumaric acid is but slightly soluble, whereas the chlorosuccinic acid is very soluble. The fumaric acid was collected and weighed, whilst the filtrate was submitted to slow evaporation and the soluble acid crystallised fractionally. It was not found possible to procure a specimen entirely free from fumaric acid, notwithstanding the great difference in their solubility, owing to the dissociation of the acid into fumaric acid and hydrogen chloride. The fumaric acid was identified by analysis and by examination of the silver salt, also by reduction to ordinary succinic acid.

Analysis gave the following numbers:

	Experiment I.	Calculated.
Carbon	40·84	41·38
Hydrogen	3·43	3·46

The silver salt when heated gives off a puff of gas and leaves a characteristic sooty residue; the silver was therefore not estimated by ignition, but by precipitation as chloride.

	Experiment.	Calculated.
Ag	65·01	65·43

Several samples of chlorosuccinic acid were analysed, but in all the percentage of chlorine was below the theoretical.

The formula, $C_4H_5ClO_4$, requires Cl = 23·25 per cent.

Specimen I left a considerable residue of fumaric acid when redissolved in water; m. p. 169°; 19·54 per cent. Cl.

Specimen II. m. p. 172°; 21·90 per cent. Cl.

Specimen III. m. p. 177°; 21·08 per cent. Cl.

Specimen IV. m. p. 171°; 21·90 per cent. Cl.

Specimen IV was used for determination of the rotatory power. After recrystallisation by evaporation in a vacuum, the melting point was 174°. It seemed impossible to secure a constant melting point, inasmuch as fusion of the acid is accompanied and probably preceded by evolution of hydrogen chloride. The residue after complete fusion continues to give off gas and finally leaves a solid infusible residue of fumaric acid.

A *silver salt* was prepared by adding silver nitrate in excess to an aqueous solution of the acid, filtering to remove a trifling precipitate of chloride and then exactly neutralising by solution of ammonia. It forms a white granular precipitate which is very slowly discoloured by exposure to day-light and is very easily soluble in ammonia and in nitric acid. It gave 58·49 per cent. of silver instead of 58·93 the percentage required by the formula. A *copper salt* similarly prepared forms a pale blue precipitate resembling cupric succinate.

l-Chlorosuccinic acid crystallises in hard and lustrous short prisms, the form of which is not yet determined.

The rotatory power determined by means of a Laurent half shade polarimeter, using a solution in water containing 9·3 grams in 100 c.c. of solution, and at a temperature of 19°, was found to be $[\alpha]_D = -19·67°$. The values given by Walden for the corresponding dextrorotatory acid were $[\alpha]_D = +20·6°$ for a solution containing 16 grams and +20·8° for a solution containing 6·4 grams per 100 c.c.

LIII.—*A Constituent of Persian Berries.*

By A. G. PERKIN, F.R.S.E., and J. GELDARD.

PERSIAN berries, as is well known, are the fruit of various species of Rhamnus, such as *R. infectoria*, *tinctoria*, &c., and are used for the production of a useful yellow colour upon various fabrics.

By the investigations of Gellatly (*Jahr.*, 1858, 474), Kane (*Berz. Jahr.*, **24**, 505), and subsequently Schützenberger (*Jahr.*, 1868, 774), these berries were shown to contain a crystalline glucoside, named xanthorhamnin, or α-rhamnegin. This glucoside, when boiled with dilute acids (Liebermann and Hörmann, *Annalen*, 1879, **196**, 307), is decomposed into isodulcite and a colouring matter, rhamnetin, to which the formula $C_{12}H_{10}O_5$ was assigned. Somewhat later Herzig (*Monatsh.*, **9**, 548—561) found that by the action of hydriodic acid on rhamnetin it yielded methylic iodide and quercetin, the colouring matter of quercitron bark, and from these results it appeared, therefore, to be a quercetin dimethyl ether, quercetin being then considered to have the formula $C_{24}H_{16}O_{11}$. More recently the same author (*Monatsh.*, **12**, 172—176) has shown that quercetin is most probably represented as $C_{15}H_{10}O_7$, from which it follows that rhamnetin is a quercetin monomethyl ether, $C_{16}H_{12}O_7$. A further proof of this relationship is afforded by the fact that quercetin and rhamnetin yield respectively a pentacetyl and a tetracetyl compound. That rhamnetin could not be considered the sole colouring matter of Persian berries was indicated by Lefort (*Jahr.*, 1866, 650), and subsequently by Schützenberger (*loc. cit.*). This latter chemist extracted from Persian berries two glucosides, namely, α-rhamnegin (xanthorhamnin), which, by decomposition with acids, yielded rhamnetin, and β-rhamnegin yielding in a similar manner a colouring matter, differing from rhamnetin, in that it was more soluble in alcohol and acetic acid; this he named β-rhamnetin. Herzig (*Monatsh.*, **10**, 561—567), who examined this subject, extracted from Persian berries a glucoside which differed from xanthorhamnin in that the colouring matter formed by the action of acids gave an acetyl derivative which melted at 169—171°, acetylrhamnetin itself melting at 183—185°. He separated this colouring matter by means of alcohol into rhamnetin and quercetin, and therefore considered the glucoside from which they were derived to be a loose double compound of xanthorhamnin and a glucoside of quercetin. This he named rhamnin. It thus appeared that the β-rhamnetin of Schützenberger was identical with quercetin.

During the study of certain acid compounds of the natural yellow colouring matters, an account of which by one of us and Mr. L. Pate will be shortly communicated to the Society, it was necessary to prepare some quantity of rhamnetin. For this purpose, we applied to Messrs. Sordes, Huillard, and Co., who very kindly gave us some quantity of a product prepared by them, and known as "rhamnétine." To purify this substance, it was extracted with a large volume of boiling alcohol, in which it was very sparingly soluble, the extract evaporated to one-fourth its bulk, and the yellow mass which separated out on cooling was recrystallised. An examination of this purified product revealed the fact that it consisted of two substances, namely, rhamnetin, and a second substance more readily soluble in acetic acid. To isolate the latter, the yellow mass was made into a thin cream with acetic acid, and the mixture boiled and rapidly filtered. The orange-brown filtrate, on cooling, deposited yellow needles contaminated with some gelatinous matter; these were collected and recrystallised from the same solvent. Recrystallisation from acetic acid did not entirely remove the gelatinous impurity, but a final recrystallisation from toluene was effectual. The product, which formed a glistening mass of pale yellow needles, melted at 214—215°, and could be neither quercetin nor rhamnetin, as these both melt with decomposition above 280°.

It was subsequently found that by extracting the commercial rhamnetin with 10 times its volume of boiling toluene for about six hours, this new substance could be more rapidly isolated. The extract, on cooling, deposited brown needles, which were collected, more being obtained on evaporating and cooling the filtrate. The product was purified by crystallisation from acetic acid and toluene, with the aid of animal charcoal.

On analysis the following numbers were obtained.

0.1238 gave 0.2811 CO_2 and 0.0468 H_2O. C = 61.92. H = 4.20.
$C_{17}H_{14}O_7$ requires C = 61.82; H = 4.24 per cent.

This substance, for which the name *rhamnazin* is proposed, forms a mass of yellow needles, somewhat resembling anthraquinone, and of considerably larger size and greater beauty than those obtained from quercetin and rhamnetin by the usual methods. When heated, it melts at 214—215° with slight decomposition, and when destructively distilled yields a small quantity of a crystalline distillate, which appears to consist of unchanged substance. Numerous preparations all melted at the same temperature. It is moderately soluble in boiling toluene, a property which distinguishes it from both quercetin and rhamnetin, moderately soluble in boiling acetic acid, but less so than quercetin, and very sparingly soluble in alcohol, in which it resembles rhamnetin, which, however, is very sparingly soluble also in acetic acid. It crystallises from acetic acid in lustrous, yellow needles, which, on drying at 100°, become opaque, with loss of one molecule of acetic acid of crystallisation.

0.6675 substance air dried lost at 100° 0.1030 gram. $C_2H_4O_2$ = 15.43.
$C_{17}H_{14}O_7 \cdot C_2H_4O_2$ requires $C_2H_4O_2$ = 15.38 per cent.

Rhamnazin dissolves in alkalis forming orange-red solutions, which, on treatment with lime water or baryta water, yield orange-red insoluble precipitates. An insoluble lead compound of the same colour is obtained on adding lead acetate to an alcoholic solution of the substance. The alcoholic solution is coloured olive-green by ferric chloride.

Action of Acetic Anhydride.—One gram of the substance, 1½ grams of anhydrous sodium acetate, and 3 grams of acetic anhydride were digested at the boiling temperature for one hour; the mixture was then treated with water and allowed to stand 24 hours, with occasional stirring. The nearly colourless powder thus obtained was collected, washed with water, drained upon a porous tile, and dried at 100°. After rinsing with a little ether, it was purified by two or three crystallisations from alcohol.

0.1394 gave 0.3102 CO_2 and 0.0545 H_2O. C = 60.68. H = 4.34.
$C_{17}H_{11}O_7(C_2H_3O)_3$ requires C = 60.53; H = 4.38 per cent.

It consisted of a colourless mass of glistening needles melting at 154—155°. Acetylrhamnetin melts at 183—185; acetylquercetin at 189—191°. Cold aqueous solutions of the alkali hydroxides do not dissolve it, but on boiling it is decomposed, with formation of a yellow solution.

Action of Benzoyl Chloride.—The benzoyl derivative of rhamnazin was prepared by the method of Baumann and Schotten, using a 10 per cent. solution of caustic soda; the colourless, viscous precipitate produced was collected upon calico, washed first with dilute, caustic soda solution, and then with water, drained upon a porous tile, and dried over sulphuric acid. It was obtained pure by crystallisation from acetic acid.

0·1146 gave 0·2977 CO_2 and 0·0412 H_2O. C = 70·84; H = 3·99.

$C_{17}H_{11}O_7(C_7H_5O)_3$ requires C = 71·02; H = 4·05 per cent.

$C_{17}H_{12}O_7(C_7H_5O)_2$ „ C = 69·12; H = 4·09 „

It was evidently therefore a tribenzoyl derivative, and the preceding substance consequently a triacetyl derivative. From acetic acid, in which it is very sparingly soluble, it is deposited in minute, colourless needles melting at 204—205°.

Action of Bromine.—Finely powdered rhamnazin, made into a thin paste with acetic acid, was treated with rather more than the theoretical quantity of bromine necessary for the formation of a dibromo-derivative. The action took place somewhat slowly, so that the mixture was allowed to stand for 48 hours, with occasional stirring, and the yellow product, after washing with glacial acetic acid, was crystallised from a large excess of the same solvent; the fine hair-like needles which separated on cooling were collected, washed with acetic acid, and dried. This substance was more rapidly produced by heating rhamnazin, suspended in carbon bisulphide, with bromine, at 100° for six hours.

0·1450 substance gave 0·1884 AgBr. Br = 32·75.

$C_{17}H_{12}O_7Br_2$ requires Br = 32·78 per cent.

It forms a silky mass of pale, yellow needles, very sparingly soluble in alcohol and in acetic acid. When heated, it begins to decompose at 250°, before melting.

Action of Hydriodic acid.—To determine if rhamnazin contained methoxy-groups, it was treated with hydriodic acid in Zeisel's apparatus in the usual manner.

0·2840 gave 0·4030 AgI. CH_3 = 9·06 per cent.

$C_{15}H_8O_5(OCH_3)_2$ requires CH_3 = 9·09 per cent.

It therefore contained two methoxy-groups. The residual hydriodic acid, in which a crystalline product was suspended, was treated with water, collected upon glass wool, washed with water, and crystallised from dilute alcohol. It formed a mass of fine yellow needles, readily soluble in alcohol.

0·1283 dried at 160° gave 0·2790 CO_2 and 0·0374 H_2O; C = 59·3; H = 3·24.

$C_{15}H_{10}O_7$ requires C = 59·60; H = 3·31 per cent.

This substance had the reactions of quercetin, and to confirm this fact it was converted into its acetyl derivative by heating with anhydrous sodium acetate and acetic anhydride in the usual manner. A product was obtained which crystallised from alcohol in colourless needles melting at 189—191°, and evidently consisted of pentacetylquercetin.

Rhamnazin is consequently a *quercetin dimethyl ether*, which result is in accordance with its formation of triacetyl and tribenzoyl compounds.

Dyeing Properties.

Experiments were instituted on the dyeing properties of rhamnazin, using striped, mordanted calico, dyeing at the same time with equal weights of quercetin and rhamnetin for comparison. The results were interesting, for although quercetin and rhamnetin both dyed readily, rhamnazin, on the other hand, showed but faint indication of dyeing power, the iron mordant being coloured a pale brown, and the alum mordanted portion showing only a faint yellow tinge. These results were not affected by the addition to the bath of 4 per cent. of acetate of lime, calculated on the weight of colouring matter employed. That this could not be due to a difference in solubility was evident, for rhamnetin is more insoluble than rhamnazin.

Quercetin, being a colouring matter, must be considered to have at least two hydroxyl groups in the ortho-position relatively to one another, and the above dyeing results point to the fact that in rhamnazin or quercetin dimethyl ether a methoxy-group is substituted for one at least of these two hydroxyl groups; the second methoxy-group present may possibly occupy a position similar to that contained in rhamnetin.

The rhamnazin used in the above experiments was obtained from the commercial product "rhamnétine," and as we had no information as to the method by which the latter was prepared from the berries, it appeared desirable to make some experiments, starting direct from Persian berries themselves. It has long been known that if a cold aqueous extract of Persian berries be heated to 30—40°, a yellow powder is quickly deposited, due to a glucoside decomposition, and that this is probably caused by a peculiar ferment has been shown by Ward and Dunlop (*Annals of Botany*, 1889). The ground berries contained in a calico bag were placed in about ten times their bulk of water at 40°; an orange-brown liquid was thus produced, from which a yellow powder soon separated, and when this precipitate no longer increased in quantity and had settled, the clear liquid was removed by decantation, and placed aside for subsequent examination. The yellow precipitate was collected, washed with water, and dried at 100°. By digesting this product with boiling toluene, an extract was obtained, which, on cooling, deposited brown needles; these were collected and purified by crystallisation from acetic acid and toluene.

0·1263 gave 0·2870 CO_2 and 0·0510 H_2O. C = 61·97; H = 4·48.
$C_{17}H_{14}O_7$ requires C = 60·86; H = 4·85 per cent.

The substance crystallised in yellow needles melting at 214—215°, and was identical with the rhamnazin previously described. The residue that had been already extracted with toluene was crystallised from a large bulk of boiling alcohol, the mother liquor being reserved for examination. It was further purified by two or three crystallisations from acetic acid with the aid of animal charcoal.

0·1262 dried at 160° gave 0·2818 CO_2 and 0·0435 H_2O; C = 60·89: H = 3·83.
$C_{16}H_{12}O_7$ requires C = 60·75; H = 3·79 per cent.

This product appeared as a glistening mass of fine, yellow needles, which melted above 280°, and were most sparingly soluble in alcohol and acetic acid. It was evidently *rhamnetin*.

The alcoholic mother liquors obtained during the purification of the rhamnetin were evaporated to one-fourth their bulk, allowed to stand 48 hours, and the small quantity of rhamnetin which had then separated was filtered off, and the filtrate evaporated to a very small bulk. The crystalline product deposited on cooling was collected, and purified by crystallisation, first from dilute alcohol, and finally from a mixture of ether and chloroform. There was thus obtained a glistening mass of minute, yellow needles melting above 280°, readily soluble in alcohol and acetic acid, and having all the reactions of *quercetin*. The amount of this substance accompanying the rhamnazin and rhamnetin in the yellow fermentation product is extremely small.

The brown, aqueous filtrate from which the mixed rhamnetin, rhamnazin, and quercetin had been deposited by fermentation, when boiled with the addition of dilute sulphuric acid and cooled, deposited some quantity of a greenish-yellow precipitate, which was collected, washed, and dried. This product, being readily soluble in alcohol, was recrystallised twice from this solvent, and to obtain it in a finely divided condition it was dissolved in hot dilute ammonia, and reprecipitated with acid. It was purified by crystallisation from a mixture of ether and chloroform, and dried at 160°.

0·1185 gave 0·2593 CO_2 and 0·0365 H_2O. C = 59·67; H = 3·42.
$C_{15}H_{10}O_7$ requires C = 59·60; H = 3·33 per cent.

Crystallised from dilute alcohol, it appeared as a glistening mass of minute yellow needles, readily soluble in alcohol and acetic acid. Its acetyl derivative, obtained in the usual manner, consisted of colourless needles melting at 189—191°. It was therefore *quercetin.* A considerable quantity was obtained in this manner.

These results are interesting, and show that xanthorhamnin, together with the unknown glucoside of rhamnazin, are readily decomposed at 40° by the ferment present in the berries. This, on the other hand, exerts but little influence on the glucoside of quercetin (quercitrin ?) which is also present.

The colouring matters obtainable from Persian berries are therefore rhamnetin or *quercetin monomethyl ether*, $C_{16}H_{12}O_7$, rhamnazin or *quercetin dimethyl ether*, $C_{17}H_{14}O_7$, and quercetin, $C_{15}H_{10}O_7$, itself.

That rhamnazin cannot be considered to be Schützenberger's β-rhamnetin is clear, on account of its sparing solubility in alcohol, and it appears evident therefore that β-rhamnetin must be quercetin, as already indicated by Herzig (*loc. cit.*). It is our intention to continue the study of Persian berries, with the hope of isolating from them the glucosides of rhamnazin and quercetin. The decomposition products obtained from rhamnazin by the action of various reagents are also undergoing investigation.

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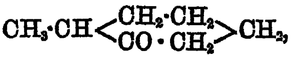
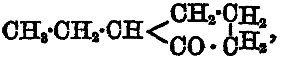
LIV.—*Paraheptotoluene and its Derivatives.*

By F. STANLEY KIPPING, Ph.D., D.Sc. and O. F. RUSSELL.

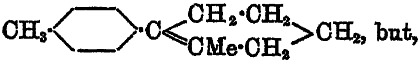
In a recent paper (*Trans.*, 1894, **65**, 480), it was shown by one of us that phenylpropionic chloride may be directly converted into hydrindone by the action of aluminium chloride, and that under suitable conditions this process affords an excellent method for the preparation of this ketone. As this was the first case in which an action of the kind had been studied and, as it appeared desirable to extend its application, experiments with other acid chlorides were commenced, and in the first place the action of aluminium chloride on heptoic chloride was investigated. This particular compound was chosen, not so much because it seemed the one most likely to undergo the desired change, but because, if it had done so, and had led to the formation of methylketohexamethylene,  $CH_3\cdot CH<\begin{matrix}CH_2\cdot CH_2\\ CO\cdot CH_2\end{matrix}>CH_2$, or of ethylketopentamethylene,  $CH_3\cdot CH_2\cdot CH<\begin{matrix}CH_2\cdot CH_2\\ CO\cdot CH_2\end{matrix}$, as seemed possible, the results would have been of considerable interest.

The first experiments were not successful; for although on warming heptoic chloride with aluminium chloride a very vigorous action occurred, and dense fumes of hydrogen chloride were evolved, most of the acid chloride was ultimately recovered in the form of heptoic acid and only a very small quantity of a neutral oil was produced; this oil, moreover, was evidently of a complex character and no definite compound was isolated from it. As, however, the previous investigation of this reaction in the case of phenylpropionic chloride had shown that so much depended on the conditions under which the substances are brought together, these unsatisfactory results were not taken as conclusive, and one of us (Russell) undertook a series of experiments to ascertain the effect of a change of temperature and of using different diluents; it was thus found that when "light petroleum" boiling at 100—110° was employed as a diluent a considerable proportion of the heptoic chloride was converted into a neutral oil, from which a crystalline compound was ultimately isolated by fractional distillation. This product was found to be a ketone of the composition $C_{14}H_{20}O$, and at first we thought that it had been formed from the heptoic chloride in accordance with the equation $2C_6H_{13}\cdot COCl = C_{14}H_{20}O + 2HCl + H_2O + H_2$.

Further investigation, however, proved it to be a paraheptotoluene of the constitution $CH_3\cdot C_6H_4\cdot CO\cdot[CH_2]_5\cdot CH_3$, and it was finally ascertained that its formation under the conditions mentioned above was due to the fact that the "light petroleum" used as a diluent accidentally contained toluene.

In this paper, therefore, we simply give an account of various compounds, which were prepared and analysed in the course of these experiments, and which have not hitherto been described; the original object of this investigation, namely the conversion of heptoic chloride into a ketone by the elimination of hydrogen chloride, has not been attained, and as it has recently come to our knowledge that Combes has already succeeded in preparing triethylphloroglucinol from butyric chloride under similar conditions (*Compt. rend.*, 1894, **118**, 1336), further experiments will not be made.

Having had at our disposal a considerable quantity of paraheptotoluene, we have investigated its behaviour with phosphoric anhydride and found that at its boiling point the ketone is converted into a hydrocarbon of the composition $C_{14}H_{18}$; this compound has probably the constitution



$CH_3\cdot C_6H_4\cdot C{<}\genfrac{}{}{0pt}{}{CH_2\cdot CH_2}{CMe\cdot CH_2}{>}CH_2$, but, as its further study had to be abandoned, we cannot put forward any very conclusive evidence in support of this view.

In the course of these experiments, laurobenzone

$$C_6H_5\cdot CO\cdot[CH_2]_{10}\cdot CH_3$$

was also prepared in order to try and convert it into a hydrocarbon similar in constitution to that obtained from paraheptotoluene; this compound was also acted on by phosphoric anhydride but the hydrocarbon thus produced was not obtained in a state of purity.

Preparation of Heptoic Chloride.

Heptoic chloride is easily prepared by mixing the acid (100 grams) with the theoretical quantity of phosphorus pentachloride (160 grams), the application of heat not being required to complete the action. Care is necessary in distilling off the phosphorus oxychloride as, under ordinary atmospheric pressure, a considerable quantity of a black tarry residue may be produced if operating with large quantities. For this reason it is best to fractionate under a pressure of about 350 mm. at first; the portion passing over between 90 and 100° consists of almost pure oxychloride, but that collected between 100 and 130° contains a little heptoic chloride and is redistilled in a subsequent operation; as soon as the thermometer rises to about 130°, the pressure is lowered to about 90 mm., whereupon the remainder of the acid chloride passes over at 108—110° without bumping. The yield is about 95 per cent. of the theoretical.

Heptoic chloride is a moderately mobile oil, having an excessively disagreeable and irritating odour; it seems to be readily decomposed by water.

Paraheptotoluene, $CH_3{\cdot}C_6H_4{\cdot}CO{\cdot}[CH_2]_5{\cdot}CH_3$.

For the sake of comparison with the ketone which, it was at first thought, had been produced from heptoic chloride alone, some paraheptotoluene was afterwards prepared by a simpler method, namely by treating pure toluene with heptoic chloride in presence of aluminium chloride, a reaction which has been previously employed by Krafft for the preparation of various ketones of this kind (*Ber.*, 1885, **19**, 2982; 1887, **21**, 2266).

Heptoic chloride (35 grams) was mixed in a large flask with a slight excess of the theoretical quantity of toluene, aluminium chloride (about 50 grams) added, and the flask connected with a reflux apparatus. Action commenced almost immediately at ordinary temperatures, and continued vigorously for about 5—8 minutes, after which time the evolution of hydrogen chloride slackened; the flask was then heated on a metal bath for about 20—25 minutes to complete the action. The dark brown product was allowed to cool, carefully treated with water, and the supernatant oil—which had partially solidified—extracted with ether; after washing well successively with sodium carbonate solution and water, the ethereal extract was dried, the ether evaporated, and the residual oil distilled under the ordinary pressure; as soon as a small quantity of toluene had passed over, the thermometer rose at once to 297°, at which temperature practically the whole of the paraheptotoluene distilled as a pale yellow oil, which on cooling solidified to a mass of colourless crystals. The yield was about 90 per cent. of the theoretical.

This ketone was found to be identical with that obtained in the earlier experiments in which the impure "light petroleum" had been used; analyses of the first preparations gave the following results.

0·1590 gave 0·4792 CO_2 and 0·1463 H_2O. C = 82·2; H = 10·2.
0·1568 gave 0·4715 CO_2 and 0·1415 H_2O. C = 82·0; H = 10·0.
$C_{14}H_{20}O$ requires C = 82·3; H = 9·8 per cent.

Paraheptotoluene (hexyl paratolyl ketone) crystallises in colourless, waxy plates, melting at 42—43°; it dissolves freely in all ordinary organic solvents, and is best recrystallised from dilute alcohol or acetone. When a few drops of bromine are added to a solution of the pure ketone in dry chloroform, cooled to 0°, a brown coloration is produced, but no evolution of hydrogen bromide occurs; even after keeping for some time and then allowing the solution to evaporate at ordinary temperatures, the ketone is recovered unchanged; if, however, it be treated at ordinary temperatures with bromine without using a solvent, action takes place slowly, and a yellowish, oily, brown derivative is formed.

Paraheptotoluene is slowly oxidised by boiling dilute nitric acid, yielding a crystalline product which consists of a mixture of terephthalic and paratoluic acids; the terephthalic acid was identified by its characteristic properties, by analysis, and by conversion into its ethylic salt (m. p. 43·5—44°) and methylic salt (m. p. 138°); the paratoluic acid was not analysed, but it was identified by its ordinary properties and by the fact that it was converted into terephthalic acid on oxidation with alkaline potassium permanganate. The ketone is only very slowly oxidised by a boiling aqueous solution of potassium permanganate, but in this case the solid oxidation product consists only of terephthalic acid.

Paraheptotolueneoxime, $CH_3{\cdot}C_6H_4{\cdot}C(NOH){\cdot}[CH_2]_5{\cdot}CH_3$.

Before it had been ascertained that the ketone described above had been produced by the interaction of heptoic chloride and toluene, its oxime was prepared and treated with concentrated sulphuric acid; the substituted amide thus obtained was then hydrolysed with dilute sulphuric acid and the products examined. As these proved to be heptoic acid and paratoluidine, the substituted amide must have had the constitution $CH_3{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}[CH_2]_5{\cdot}CH_3$, and consequently the original ketone must have been paraheptotoluene.

The oxime was prepared by treating the pure ketone with hydroxylamine hydrochloride and excess of soda in aqueous alcoholic solution at the ordinary temperature; after evaporating the alcohol, the oily product was extracted with ether and the dried, filtered extract evaporated. A portion of the oil which had been kept over sulphuric acid under reduced pressure was analysed.

0·1591 gave 0·4400 CO_2 and 0·1434 H_2O. C = 75·4; H = 10·0.

0·1962 „ 10·8 c.c. of moist nitrogen at 16° and 765 mm. N = 6·75 per cent.

$C_{14}H_{21}NO$ requires C = 76·71. H = 9·59; N = 6·39 per cent.

Paraheptotolueneoxime is a rather thick oil, insoluble or nearly so in water, but slightly soluble in potash; it dissolves freely in the ordinary organic solvents, and it interacts readily with acetic chloride with development of heat; it is also soluble in concentrated sulphuric acid.

Paraheptotoluidide, $CH_3\cdot C_6H_4\cdot NH\cdot CO\cdot[CH_2]_5\cdot CH_3$.

The conversion of the oxime into the isomeric substituted amide was readily accomplished, by warming it on the water bath with four times its weight of concentrated sulphuric acid for about 10 minutes; when the operation was continued much longer, the solution darkened, traces of sulphur dioxide were evolved, and the product was coloured. After pouring the solution into a large volume of water, the amide, which was first precipitated as an oil but rapidly solidified, was separated by filtration and recrystallised from alcohol.

0·1813 gave 0·5063 CO_2 and 0·1588 H_2O. C = 76·2; H = 9·7.

$C_{14}H_{21}NO$ requires C = 76·7. H = 9·6.

Paraheptotoluidide crystallises from hot dilute alcohol in colourless, transparent, rather waxy plates, and from a mixture of ether and light petroleum in concentrically grouped needles; it melts at 78—79°, and dissolves freely in all ordinary organic solvents with the exception of light petroleum, in which it is only moderately easily soluble.

On hydrolysis with moderately concentrated (1 : 1) boiling sulphuric acid, paraheptotoluidide is resolved into its components, heptoic acid and paratoluidine; the base was identified by analysis by comparison with a sample of paratoluidine, and by converting it into acetoparatoluidide. Some paraheptotoluidide was also prepared by warming paratoluidine with heptoic chloride; this preparation was found to be identical with that obtained from the oxime of paraheptotoluene.

Hydrocarbon, $C_{14}H_{18}$.

It has already been mentioned that a hydrocarbon of the composition $C_{14}H_{18}$ may be obtained by heating paraheptotoluene with phosphoric anhydride; the following is the method employed.

The pure, dry ketone, in quantities of about 10 grams at a time, was heated to boiling in a flask provided with a reflux apparatus, and rather more than one molecular proportion of phosphoric anhydride gradually added, the contents of the flask being vigorously shaken after each addition in order to prevent the anhydride from caking at the bottom of the vessel; after boiling for about 25 minutes and then allowing to cool, the very dark mass was treated with water and submitted to distillation in steam. The oil in the distillate was separated, dried, and fractionated under ordinary atmospheric pressure; 41 grams of the crude product, which had been obtained from 60 grams of the ketone, yielded the following fractions:—Below 260° (5 grams), 260—265° (22 grams), 265—270° (8 grams), 270—278° (6 grams). The second and third fractions were again distilled, and finally a considerable quantity of an oil boiling constantly at 260—262° was obtained; this product was analysed with the following results.

0·1447 gave 0·4765 CO_2 and 0·1336 H_2O. C = 89·8; H = 10·2.
0·1443 „ 0·4728 CO_2 and 0·1310 H_2O. C = 90·0; H = 10·2.
$C_{14}H_{18}$ requires C = 90·3. H = 9·7.

This hydrocarbon was of a pale yellow colour, and showed a faint violet fluorescence, probably due to traces of impurity; it did not solidify when cooled to 0°, and was more mobile than the ketone from which it was derived; it had a faint odour recalling that of petroleum.

Several experiments were made in the hope of obtaining some evidence in favour of the constitutional formula suggested above, and although the results were by no means conclusive, they certainly indicated that the hydrocarbon was not an unsaturated compound of the constitution $CH_3{\cdot}C_6H_4{\cdot}C{\vdots}C{\cdot}[CH_2]_4{\cdot}CH_3$. When, for example, the hydrocarbon was dissolved in chloroform, the solution cooled in a freezing mixture, and a cold chloroform solution of bromine cautiously added, a rapid evolution of hydrogen bromide set in long before one molecular proportion of the halogen had been run in, only the first few drops being immediately decolorised; the products obtained in various experiments of this kind, employing different quantities of bromine, did not crystallise, and were not analysed. Towards oxidising agents also, the hydrocarbon did not behave as if it contained an acetylenic linking as it was comparatively slowly acted on; when boiled with dilute nitric acid, it was converted into terephthalic acid and a yellow, resinous product from which no definite compound was isolated; similar results were obtained on employing an alkaline solution of potassium permanganate.

Laurobenzene, $C_6H_5\cdot CO\cdot[CH_2]_{10}\cdot CH_3$.

Laurobenzene was easily prepared by treating lauric chloride with benzene and aluminium chloride under conditions similar to those employed in the case of paraheptotoluene; the lauric chloride used for this purpose contained phosphorus oxychloride, as it was found inexpedient to separate the whole of the latter owing to the darkening which occurred during the fractional distillation after about four-fifths of the oxychloride had passed over.

The dark product obtained after heating the benzene solution of the acid chloride with aluminium chloride until the evolution of hydrogen chloride was practically at an end was repeatedly treated with water to dissolve out the aluminium chloride and the pasty mass was then shaken vigorously with warm, concentrated potash; after allowing it to settle, the solution of potassium laurate was siphoned off from the semi-solid, supernatant layer of laurobenzene. This treatment having been repeated several times, the laurobenzene was dissolved in ether, the solution washed with potash and water successively, dried, and evaporated; the oily residue rapidly solidified, and, after having been spread on porous earthenware, was purified by recrystallisation from alcohol.

Laurobenzene crystallises in colourless, rather waxy plates melting at about 47°; it is readily soluble in cold petroleum, ethylic acetate, and other organic liquids, but insoluble in water.

When laurobenzene was heated with phosphoric anhydride, it rapidly darkened, but, even after boiling it with a slight excess of the anhydride for about 20 minutes, only a part of it was converted into a hydrocarbon. The product, isolated by distillation in superheated steam, was a yellow oil which did not crystallise at 0°; on fractional distillation, under ordinary pressure, it began to boil at about 325°, and the temperature then rose slowly to about 350°; even after repeated fractionation, it still contained unchanged ketone, and gave unsatisfactory results on analysis.

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LV.—*Methylisobutylacetic acid*, $CH(CH_3)_2·CH_2·CH(CH_3)·COOH$.

By M. W. BURROWS, B.Sc., and W. H. BENTLEY, B.Sc.

In a recent paper on $\beta\beta$-methylethylpropionic acid (this vol., 264), it was pointed out that the object of the work was to obtain by synthesis some of the fatty acids which had not been previously described, and to compare their properties with those of some fatty acids of unknown constitution derived from camphoric acid by fusion with potash. With this same object in view, we have prepared and investigated the properties of methylisobutylacetic acid under the direction of Dr. Perkin, the results of the investigation forming the subject of the present paper.

The acid was obtained from ethylic malonate in two ways, which however only differed in the order of insertion of the groups methyl and isobutyl. By one method, ethylic isobutylmalonate,

$$CH(CH_3)_2·CH_2·CH(COOEt)_2,$$

was prepared by the action of isobutylic bromide on ethylic sodiomalonate, and this was converted into ethylic methylisobutylmalonate, $CH(CH_3)_2·CH_2·C(CH_3)(COOEt)_2$, by treating its sodium derivative with methylic iodide. By the second method, ethylic sodiomethylmalonate was acted on by isobutylic bromide, the product being (as before) ethylic methylisobutylmalonate. Judging from the subsequent yield of acid, the former method seems to give rather better results.

Ethylic methylisobutylmalonate is an oil which boils at 230—235°, and, on hydrolysis, yields methylisobutylmalonic acid,

$$CH(CH_3)_2·CH_2·C(CH_3)(COOH)_2,$$

a solid, melting at 122°; this, in its turn, is decomposed on distillation, losing carbon dioxide and yielding methylisobutylacetic acid, $CH(CH_3)_2·CH_2·CH(CH_3)·COOH$. The pure acid boils at 204—205° under a pressure of 755 mm.

For the purpose of identification, the following derivatives of methylisobutylacetic acid have been prepared.

Ethylic salt, $C_6H_{13}·COOEt$; an oil boiling at 165—166° (769 mm.).

Acid chloride, $C_6H_{13}·COCl$; a pungent-smelling liquid boiling at 152—153° (745 mm.).

Amide, $C_6H_{13}·CO·NH_2$; a colourless solid crystallising from ether in needles melting at 90°.

Anilide, $C_6H_{13}·CO·NH·C_6H_5$; a colourless solid crystallising from high boiling, light petroleum in long, silky needles melting at 110—111°.

Paratoluidide, $C_6H_{13}\cdot CO\cdot NH\cdot C_7H_7$; a colourless solid separating from low boiling light petroleum in minute needles melting at 86°.

EXPERIMENTAL PART.

Methylisobutylmalonic acid, $CH(CH_3)_2\cdot CH_2\cdot C(CH_3)(COOH)_2$.

The details of the first method of preparation are as follows.

Isobutylic bromide (109 grams) was added to a mixture of ethylic malonate (127 grams) with a solution of sodium (18·5 grams) in alcohol (200 grams), and the whole heated on the water bath until the mixture was perfectly neutral. When cold, it was diluted with water, and the oil extracted with ether; the ethereal solution was then washed with water, dried with calcium chloride, and the ether distilled off on the water bath. The oily residue was fractionated, and the portion boiling at 224—226° (105 grams), and consisting of pure ethylic isobutylmalonate, was added to a solution of sodium (11·1 grams) in alcohol (150 grams), and treated with methylic iodide (70 grams). The mixture was heated on the water bath till neutral, and afterwards subjected to the same treatment as before, the final product being ethylic methylisobutylmalonate, $CH(CH_3)_2\cdot CH_2\cdot C(CH_3)(COOEt)_2$. It boils at 230—235°, and the yield was 86 grams.

This oil was not analysed, but at once saponified by boiling with an excess of alcoholic potash, the alcohol being afterwards removed by diluting with water and evaporating the liquid to dryness; the solid residue was then dissolved in water, acidified strongly, and repeatedly extracted with ether. After distilling off the ether, a viscous liquid remained, which solidified, however, on standing; it was placed in a vacuum over sulphuric acid for a day, then dried on a porous plate, and purified by recrystallisation from a small quantity of water.

0·1063 gave 0·2151 CO_2 and 0·0793 H_2O. C = 55·19; H = 8·29.

$C_8H_{14}O_4$ requires C = 55·17; H = 8·05 per cent.

Methylisobutylmalonic acid melts at 122°. It is extremely soluble in water, and can only be crystallised from very concentrated solutions; it can be dried at 100° without decomposition. The silver salt was prepared by precipitating a solution of its ammonium salt with silver nitrate; after washing and drying, it was analysed by ignition.

0·1737 gave 0·0972 Ag. Ag = 55·95.

$C_8H_{12}Ag_2O_4$ requires Ag = 55·67 per cent.

It was found that the silver salt could be heated to 135° without decomposition.

Methylisobutylacetic acid, $CH(CH_3)_2 \cdot CH_2 \cdot CH(CH_3) \cdot COOH$.

The dibasic acid was heated in a retort to 195—215° when it decomposed into carbon dioxide and a fatty acid, and this acid, after repeated fractionation, was found to boil constantly at 204—205°. A second sample of the acid was prepared from ethylic malonate by introducing first the methyl group, and afterwards the isobutyl group, the details of the processes being practically the same as those given for the other method. The fatty acid obtained boiled at exactly the same temperature as did the other sample, namely, 204—205°, under a pressure of 755 mm.; the penetrating odour and general properties of this acid are similar to those of the higher fatty acids.

0·1034 gave 0·2440 CO_2 and 0·0994 H_2O. C = 64·36; H = 10·68.
$C_7H_{14}O_2$ requires C = 64·61; H = 10·77 per cent.

Ethylic methylisobutylacetate, $CH(CH_3)_2 \cdot CH_2 \cdot CH(CH_3) \cdot COOC_2H_5$.—This was prepared by saturating a solution of the acid in pure ethylic alcohol with dry hydrogen chloride, and allowing the mixture to remain for some time; water was then added, and the oil which separated extracted with ether. The ethereal solution, after being washed first with sodium carbonate, and then with water, was dried with calcium chloride, and the ether evaporated. An oil remained behind which, on fractionation, was observed to boil constantly at 165—166° (769 mm.).

Found.............. C = 68·37; H = 11·44 per cent.
Theory for $C_9H_{18}O_2$ .. C = 68·35; H = 11·39 „

Methylisobutylacetyl chloride, $CH(CH_3)_2 \cdot CH_2 \cdot CH(CH_3) \cdot COCl$.—This compound was prepared by heating 11 grams of the acid with 4 grams of phosphorus trichloride for 10 minutes in a reflux apparatus; after decanting from the heavier phosphorous acid, the liquid was fractionated. The acid chloride boils at 152—153° (745 mm.), and possesses the pungent and disagreeable odour characteristic of the higher acid chlorides. Analysis.

Found................. Cl = 24·05 per cent.
Theory for $C_6H_{13} \cdot COCl$.. Cl = 23·90 „

Methylisobutylacetamide, $CH(CH_3)_2 \cdot CH_2 \cdot CH(CH_3) \cdot CONH_2$.—This substance was obtained from the ethylic salt and also from the acid chloride.

The ethylic salt was heated with concentrated aqueous ammonia in a sealed tube at 180° for 10 hours, and the product repeatedly extracted with ether, the ethereal solution was dried with calcium chloride, the ether removed by evaporation, and the residue poured into a basin to solidify. The solid was then recrystallised first from ether and subsequently from light petroleum of high boiling point.

The acid chloride was slowly added to concentrated aqueous ammonia, the mixture extracted with ether several times, and the ethereal solution dried with calcium chloride. The amide was then extracted and purified as in the previous case. Both samples melted at 90° (a low melting point for an amide of a higher fatty acid), and crystallised from both petroleum and ether in needles.

Found.................. N = 10 70 per cent.
Theory for $C_6H_{13}\cdot CO\cdot NH_2$.. N = 10·85 „

This amide is extremely soluble in alcohol and chloroform, rather less so in ether, and sparingly in ethylic acetate, benzene, and light petroleum of low boiling point; it is insoluble in cold water.

Methylisobutylacetanilide, $CH(CH_3)_2\cdot CH_2\cdot CH(CH_3)\cdot CO\cdot NH\cdot C_6H_5$.—This anilide was prepared by boiling the acid with twice its weight of aniline for 24 hours in a reflux apparatus; the solid product was dissolved in ether, the ethereal solution washed with hydrochloric acid, then with sodium carbonate solution, and finally with water. After drying with calcium chloride, the ether was distilled off, and the dark-coloured residue purified by repeated crystallisation from petroleum (b. p. 100—120°), from which it separates in beautiful, long, silky needles melting at 110—111°.

Found...................... N = 7·10 per cent.
Theory for $C_6H_{13}\cdot CO\cdot NH\cdot C_6H_5$.. N = 6·83 „

This anilide is very soluble in ether, chloroform, benzene, ethylenic chloride, ethylic acetate, and alcohol; water precipitates it from a concentrated alcoholic solution, and it can be conveniently recrystallised from dilute alcohol. It is sparingly soluble in cold petroleum, but it dissolves readily in hot petroleum; it is insoluble in cold water.

Methylisobutylacetoparatoluidide,

$$CH(CH_3)_2\cdot CH_2\cdot CH(CH_3)\cdot CO\cdot NH\cdot C_7H_7.$$

—The preparation and purification of this substance only differed from those of the anilide in two points; the mixture of acid with 2½ times its weight of paratoluidine was heated for a shorter period (15 hours) on account of the higher boiling point of paratoluidine, and the crude product was recrystallised from light petroleum of low boiling point. It crystallises in minute needles melting at 86°.

Found...................... N = 6·19 per cent.
Theory for $C_6H_{13}\cdot CO\cdot NH\cdot C_7H_7$.. N = 6·39 „

This toluidide is very soluble in alcohol, chloroform, ether, benzene, and ethylic acetate; it is sparingly soluble in cold, but readily in hot light petroleum; it is insoluble in cold water.

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LVI.—*Note on the Formation of Platinic Pyrophosphate.*

By Robert E. Barnett, A.R.C.S.

In order to prepare phosphorus pentoxide in a state of purity, for use in a research now in progress in conjunction with Professor Tilden, recourse was had to the method described by Shenstone and Beck in this Journal for 1893 (Trans., **63**, 475). Commercial phosphorus pentoxide, placed in a platinum boat in a combustion tube, is sublimed in a current of oxygen over spongy platinum kept at a red heat in the fore part of the tube. If the heating has been moderate, the metaphosphoric acid always present remains in the boat as a glassy mass, as it is less volatile than the pentoxide. But besides this residue there was always present a certain amount of a yellow pulverulent substance, most of which remained adhering to the platinum after the metaphosphoric acid was dissolved off by water. This yellow substance was found chiefly on the outside surface of the boat, and appeared therefore to be a product of the action of vapours on the platinum rather than a non-volatile residue from the pentoxide itself. Acting on this idea, and with the view of obtaining a larger quantity, the spongy platinum which had served for several such sublimations was digested repeatedly with *aqua regia* until nothing further was dissolved. A very considerable amount of the new substance, about one-fourth of the original weight of the platinum, remained as a heavy insoluble yellow powder; after washing and drying it was submitted to analysis by fusion with $KNaCO_3$. It was found to yield nothing but platinum and phosphoric acid, and these in proportions which gave approximately the formula PtP_2O_7. It was evident on inspection, however, and from the discordant results of the analyses, that the compound was mixed with fragments of glass and asbestos from the combustion tubes, and consequently fresh sublimations were performed in the same manner, but having the platinum sponge enclosed in a cage of platinum gauze to protect it from mechanical contamination. On treating the product with *aqua regia* in the manner previously mentioned, 7 grams of the yellow substance was obtained. Curiously enough, this seems to be formed chiefly in the interior of the lumps of spongy platinum, so that before treatment with the acid the only indication of its presence is a scarcely perceptible greenish tinge on the ordinarily grey platinum. After treatment with the acid, too, the yellow substance was to a large extent in masses retaining the original form of the pieces of sponge, so that it was necessary to reduce them to powder to extract all the uncombined platinum.

This second preparation was free from visible impurity, and yielded the following results on analysis.

I. 0·8036 gave 0·4243 Pt = 52·80 Pt and 0·4937 $Mg_2P_2O_7$ = 17·11 P.
II. 0·8050 „ 0·4258 Pt = 52·89 Pt „ 0·4942 $Mg_2P_2O_7$ = 17·09 P.

$$\text{Calculated for } PtP_2O_7 = \begin{cases} 52{\cdot}82 \text{ per cent. Pt.} \\ 16{\cdot}82 \quad ,, \quad \text{P.} \end{cases}$$

The formula PtP_2O_7, which must therefore be ascribed to the substance, is obviously that of *platinic pyrophosphate*, a compound hitherto unrecorded. And although the attempts I am still making to obtain the substance by a more direct method have not yet met with success, and its properties generally are so unlike those of the oxysalts of platinum, the following reaction clearly shows its nature. If it be treated in the cold with sulphuretted hydrogen water, [illegible] slowly darkens and ultimately becomes black. The supernatant liquid gives the reactions of pyrophosphoric acid. On treating the liquid thus prepared with silver nitrate, filtering off the silver sulphide, [illegible] neutralising, a white precipitate is obtained. On analysis this yielded 70·9 per cent. Ag., the calculated percentage for silver pyrophosphate being 71·2.

Platinic pyrophosphate, prepared as above described, is a pale greenish-yellow powder, apparently amorphous; its density is 4·856. It is stable at a red heat, darkening somewhat but regaining its original colour on cooling. In contact with a flame, however, it is readily reduced, giving off white fumes. It is insoluble in water and unaffected by aqueous acids and alkalis, although easily decomposed by fusion with $KNaCO_3$. It is insoluble in a solution of sodium pyrophosphate. Chlorine and bromine appear to be without action on it. It is gradually decomposed by solutions of hydrogen sulphide or alkali sulphides.

I would state that I am continuing experiments on this and similar compounds of platinum, and in conclusion desire to record my thanks to Professor Tilden for his kind assistance in the foregoing investigation.

LVII.—*Action of Hydrogen Sulphide on Antimonic Acid Solutions.*

By OTTO BOŠEK, Ph.D.

(Communicated by Professor Bohuslav Brauner, Bohemian University, Prague.)

THE following is a condensed account of work done by Dr. Bošek under my direction in the University Laboratory at Prague.

From the analogy between arsenic and antimony, H. Rose (*Ann. Phys. Chem.*, 1859, **107**, 186) concludes that hydrogen sulphide throws down from a solution of arsenic acid or of antimonic acid a mixture of the respective trisulphides with sulphur, and that the pentasulphides of these elements can only exist in the form of sulpho-salts. Bunsen (*Annalen*, 1878, **192**, 305), on the other hand, recommends the precipitation of antimony in the form of the pentasulphide for the quantitative estimation of this element. Willm (*Zeit. anal. Chem.*, 1891, **30**, 443) obtained results differing from those of Bunsen; he treated the freshly precipitated antimony trisulphide with caustic potash and chlorine, and, after repeated evaporation with hydrochloric acid, added tartaric acid and water. and precipitated the solution at 60—70° with hydrogen sulphide. Bunsen regarded the precipitate as pure antimony pentasulphide, but if prepared in this way or by decomposing Schlippe's salt with an acid, Willm found that it invariably lost part of its sulphur 3·5—13·8 per cent.). Thiele (*Annalen*, 1891, **263**, 71) was also unable to confirm Bunsen's results as regards the formation of pure antimony pentasulphide.

Brauner and Tomíček (Trans., 1888, **53**, 145) found that on treating solutions of arsenic acid with hydrogen sulphide, either pure arsenic pentasulphide was obtained, in accordance with the statements of Bunsen, or, on varying the temperature, the rapidity of the gas current, the acidity of the liquid, &c., a mixture of the pentasulphide with the trisulphide and free sulphur was thrown down.

In the present paper, the results of a somewhat similar series of experiments are given on the action of hydrogen sulphide on antimonic acid under varying conditions.

Antimonic solutions were prepared either by dissolving the pure metal in a mixture of hydrochloric acid and potassium chlorate, or pure antimony trioxide was dissolved in caustic potash, and the solution treated with bromine or chlorine. In preliminary experiments, made with solutions prepared by the first method, it was soon found that it was most important to ascertain first whether the tervalent antimony is completely oxidised to the quinquevalent state. This examination is the object of the first series of experiments.

I. *Action of Oxidising Agents on Antimonious Salts.*—This subject has been to some extent investigated by Kessler (*Ann. Phys. Chem.*, 1855, **95**, 204, 225; **113**, 134), whose method for the determination of the state of oxidation was used.* In the present experiments, the antimony was dissolved in hydrochloric acid at 15—20° or at 70—80°, varying quantities of potassium chlorate being added. The excess of chlorate was then destroyed by evaporation, and the solution was diluted with hydrochloric acid to a definite volume.

Experiment 1.—2·502 grams of antimony were treated with 30 c.c. of hydrochloric acid, and just enough potassium chlorate added to obtain complete solution of the metal. After treating as above described, and diluting to 100 c.c., 10 c.c. of the solution were mixed with 10 c.c. of hydrochloric acid and 80 c.c. of water, in order to satisfy the conditions prescribed by Kessler. Result: Unoxidised $SbCl_3$ = 28·08 per cent. and 28·05 per cent.

Experiment 2.—1·566 grams of metallic antimony were dissolved in 50 c.c. of hydrochloric acid and 1·75 grams of potassium chlorate at the ordinary temperature. Result: Unoxidised $SbCl_3$ = 17·68 per cent. and 17·65 per cent.

Experiment 3.—1·42 grams of antimony were dissolved at 60° in 50 c.c. of hydrochloric acid and 1·50 grams of potassium chlorate. Result: Unoxidised $SbCl_3$ = 12·35 per cent. and 12·33 per cent.

The amount of oxidation increases with increase in the quantity of potassium chlorate and increasing temperature, but complete oxidation could not be brought about in this way.

On evaporating in a vacuum over sulphuric acid the solutions obtained as above, beautifully crystalline, double salts were obtained. The first kind of crystals were colourless, transparent, of a hexagonal habit, but too unstable to be measured. Analysis shows that their formula is $2KCl,SbCl_3$. The other crystals were lemon-yellow, transparent, of a monoclinic habit, but too deliquescent to be measured. Their composition corresponds with the formula

$$3KCl,2SbCl_4.$$

	Sb.	Cl.	K.
Calculated for $3KCl,2SbCl_4$	32·15	52·17	15·68
Found......................	31·29	52 38	15·38

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* Kessler determines the amount of unoxidised, that is, tervalent antimony, by titrating a solution containing 20 per cent. hydrochloric acid with standard potassium dichromate in excess, destroying that excess with a standard solution of ferrous salt, and then again adding the dichromate solution carefully until a drop of the liquid no longer gives a blue coloration with potassium ferricyanide. (For details see also Brauner, Trans., 1891, 59, 62.)

Repeated attempts were made to obtain this substance again by mixing antimony trichloride, pentachloride, and potassium chloride in different proportions and evaporating the hydrochloric solution of these constituents in a vacuum, but the crystals could not be obtained again; it is uncertain, therefore, whether they are the double compound of the new antimony tetrachloride, $SbCl_4$, or a mixture of double salts of the trichloride and pentachloride. On precipitating their solution with hydrogen sulphide, a peculiar reddish-pink sulphide was obtained, having the composition and the properties of *antimony tetrasulphide*, Sb_2S_4, described in Experiment 32.

Some experiments were made in order to ascertain to what extent the oxidation of antimony can be effected by nitric acid.

Experiment 4.—To 0·222 gram of metallic antimony, 5 c.c. of fuming nitric acid were added drop by drop, and the crucible (covered) was then heated on a water bath for three hours. After evaporating to dryness, and finally removing the last traces of nitric acid by evaporation with hydrochloric acid, the residue was dissolved in hydrochloric acid and analysed, using Kessler's potassium dichromate method. Result: Unoxidised Sb_2O_3 = 14·19 per cent.

Experiment 5.—0·2355 gram metallic antimony was treated with 10 c.c. of fuming nitric acid as above. Result: Unoxidised Sb_2O_3 = 4·87 per cent.

Experiment 6.—0 2875 gram of antimony was treated with 15 c.c. of fuming nitric acid. Result: Unoxidised Sb_2O_3 = 1·77 per cent.

From this it will be seen that it is impossible to obtain pure antimonic acid, even when a large excess of fuming nitric acid is used.

The following series of experiments were made in order to ascertain the amount of oxidation produced by bromine water in alkaline antimonious solutions. Antimony trisulphide could not be used, as it dissolves only very incompletely in caustic potash. A solution of antimony in hydrochloric acid and potassium chlorate as obtained in Experiment 1, and containing a known percentage of the metal, was therefore chosen as the starting point. This was dissolved in caustic potash, always using the same quantity, and then varying quantities of bromine water were added. After heating for a definite time on the water bath, hydrochloric acid was added, and the decomposition of the hypobromite effected by evaporation, employing the precautions mentioned by Bunsen. The amount of unoxidised Sb_2O_3 was determined by Kessler's volumetric method.

Experiment 7.—0·1263 gram of antimony in alkaline solution was heated on a water bath with 20 c.c. of bromine water for two hours, &c., as above described. Result: Unoxidised Sb_2O_3 = 12·67 per cent.

Experiment 8.—Same quantities of antimony and bromine water as in Experiment 7, but the action was continued for four hours. Result: Unoxidised Sb_2O_3 = 3 89 per cent.

Experiment 9.—Same quantities of antimony and bromine water as in Experiments 7 and 8 were employed, but the mixture was heated for 10 hours. Result: Unoxidised Sb_2O_3 = 1·51 per cent.

Experiment 10.—Same quantities as in the foregoing experiments, but the heating was continued for 12 hours. Result: The oxidation was complete.

For the following experiments, solutions of pure antimony trioxide were treated as above.

Experiment 11.—0·204 gram of pure antimony trioxide, Sb_2O_3, was dissolved in caustic potash, and heated with 30 c.c. of bromine water on a water bath for two hours, then decomposed with hydrochloric acid. Result: Unoxidised Sb_2O_3 = 14·17 per cent.

Experiment 12.—The same quantity of antimony solution as that used in Experiment 11 was heated with 30 c.c. of bromine water for 12 hours; the solution was then very gradually decomposed with hydrochloric acid. Result: Oxidation complete.

Experiment 13.—Same solution as in Experiment 7, 60 c.c. bromine water; time, one hour. Result: Unoxidised Sb_2O_3 = 17·86.

Experiment 14.—Same solution as in Experiment 11, 60 c.c. bromine water; time, one hour. Result: Unoxidised Sb_2O_3 = 15·42.

Experiment 15.—Same conditions as in Experiment 13, 50 c.c. bromine water; time, two hours. Result: Unoxidised Sb_2O_3 = 12·46. On comparing this experiment with Experiment 7, it is seen that the effect of the oxidising agent is almost entirely dependent on the time during which it acts. All the experiments show how difficult it is to bring about complete oxidation of antimony to the quinquevalent state. This important fact explains the discordant results obtained by the different authors who repeated Bunsen's experiments on the action of hydrogen sulphide on what were considered by them to be solutions of pure *antimonic* acid, but which, in reality, were mixtures of *antimonious* and *antimonic* compounds in varying proportions.

The action of these oxidising agents on antimonious compounds is at first rapid, gradually becoming much slower, and, on representing this graphically, a sharply-bent hyperbolic curve is obtained, having much the same character as the curve expressing the action of chromic action on hydrochloric solutions of tellurous acid (compare Brauner, Trans., 1891, 59, 66).

Action of Hydrogen Sulphide on Antimonic Solutions.

The following series of experiments were made with solutions of antimonic acid prepared as follows:—Antimony trioxide, pure and especially free from arsenic, was dissolved in excess of caustic potash and a rapid current of chlorine passed into the solution for 12 hours; it was then several times evaporated down with concentrated hydrochloric acid until no more chlorine was given off. In order to see whether the oxidation of the antimony was complete, a portion of the solution was examined with standard potassium dichromate, and was found to be free from every trace of antimonious acid. The solution was then diluted to 1000 c.c., but it was found impossible to determine the amount of antimony present in an aliquot part, and to use the rest for further experiments, as an amorphous, white precipitate was slowly deposited. Therefore, as a starting point for the calculation of results, pure black antimony trisulphide was used, prepared by heating any of the precipitated sulphides in a current of carbonic dioxide at 210°, the product having the definite composition Sb_2S_3 (compare Paul, *Zeit. anal. Chem.*, 1892, 31, 537). For precipitating, either gaseous hydrogen sulphide was used, or its solution made with water previously well-boiled and cooled; in order to avoid separation of sulphur, the excess of the gas was driven out by a rapid current of carbonic anhydride.

First Series of Experiments.

Experiment 16.—First of all, Bunsen's method was repeated in order to see whether really pure antimony pentasulphide is obtained in this way. 50 c.c. of the above solution were mixed with 14 grams of hydrochloric acid, the whole diluted to 100 c.c., and 200 c.c. of freshly prepared aqueous hydrogen sulphide added, stirring all the time; after removing the excess of the hydrogen sulphide, the precipitate was collected on a Gooch crucible filter, washed with water, then four times with alcohol, twice with a mixture of alcohol and carbon bisulphide, then four times with pure, redistilled carbon bisulphide, then four times with alcohol, after which it was dried at 105—107°. Result:

	A.	B.*
Weight of dried precipitate	0·2301	0·1889
Sb_2S_3 dried in CO_2 at 210°	0·1927	0·1589
Sb_2S_5 calculated from this	0·2294	0·1892
Difference	+0·0007	−0·0003

As the difference is within the limit of unavoidable experimental error, it is seen that by precipitating *completely oxidised* solutions of antimonic acid with aqueous hydrogen sulphide, *added at once*, and *at the ordinary temperature*, pure *antimony pentasulphide* is obtained. The pentasulphide is dark brown.

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* As several weeks had elapsed between Experiments A and B, for the reasons above stated, 50 c.c. of the solution did not contain the same amount of antimony.

Experiment 17.—50 c.c. of the same solution as in Experiment 16 (*i.e.*, +14 grams HCl) were precipitated by passing a rapid current of gaseous hydrogen sulphide for half an hour, and the precipitate treated as above. Result:

Weight of dried precipitate		0·2287 gram.
„ Sb_2S_3		0·1932 „
Composition of the original precipitate*	Sb_2S_3 =	3·12
	Sb_2S_5 =	96·88
		100 00

Experiment 18.—50 c.c. of the same antimonic solution (*i.e.*, +14 grams HCl) were put into a beaker and 200 c.c. of hydrogen sulphide water added drop by drop from a burette with constant stirring. Even the first three drops produced an orange-coloured precipitate which rapidly increased. Result:

Weight of dried precipitate		0·1895 gram.
„ Sb_2S_3		0·1602 „
Composition of precipitate	Sb_2S_3 =	3·32
	Sb_2S_5 =	96·68
		100·00

Conclusion.—When hydrogen sulphide acts on pure antimonic solutions for a longer time and therefore slowly, *not at once*, a partial *reduction* takes place.

In the following experiments, the influence of a larger quantity of hydrochloric acid present was studied.

Experiment 19.—50 c.c. of the same antimonic solution was acidified with 25 c.c. of hydrochloric acid, and aqueous hydrogen sulphide was added slowly from a burette. At first, free sulphur separated and produced a turbidity, and the first visible precipitate was obtained after the addition of 3 c.c. of hydrochloric acid; it took two and a half hours to add the 200 c.c. of aqueous H_2S. Result:

Weight of dried precipitate		0·1560 gram.
„ Sb_2S_3		0·1325 „
Composition of precipitate	Sb_2S_3 =	5·39
	Sb_2S_5 =	94·61
		100·00

Experiment 20.—Experiment 19 was repeated, using 40 c.c. of hydrochloric acid, no separation of orange coloured precipitate from the turbid liquid took place until after the addition of 6 c.c. of hydrochloric acid. The very pale colour of the precipitate, and the strong turbidity of the alcoholic washings showed that much free sulphur was present. In fact, it was impossible to remove it completely, and as part of the sulphur present was in the form insoluble in carbon bisulphide, it must have been produced by oxidation of the hydrogen sulphide. Result:

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* From the above two data, the difference between the amount of Sb_2S_5 calculated from the Sb_2S_3 obtained, and the weight of the original precipitate and the molecular weight of Sb_2S_3, the amount of Sb_2S_3 and Sb_2S_5 is easily calculated.

Weight of dried precipitate	0·2090	gram.
" Sb_2S_3	0·1710	"
Calculated weight of Sb_2S_5	0·2038	"
Difference	+0·0052	"

Owing to the strong reduction, 0·0052 gram of sulphur or 2·49 per cent. was found insoluble, over and above the theoretical quantity of pentasulphide, so that the percentage of Sb_2S_3 in the precipitate could not be calculated.

The present experiments show that the presence of an increased quantity of hydrochloric acid causes an increase in the reduction of the quinquevalent antimony compound, but owing to the separation of insoluble sulphur, as in Experiment 20, it is impossible to determine whether a precipitate formed in the presence of a large quantity of hydrochloric acid, is pure antimony pentasulphide, even if it *appeared* to have the same composition. From this point of view, some of the results obtained by Thiele (*Annalen*, 1891, **263**, 71) must be regarded with reserve. This author found that the quantity of antimony pentasulphide increased on increasing the amount of hydrochloric acid present from 2 to 10 per cent. It is possible that the maximum quantity of pentasulphide formed lies somewhere between 10 to 20 per cent. of hydrochloric acid, but it certainly diminishes above that limit.

Experiments at Higher Temperatures.

Experiment 21.—50 c.c. of the above antimonic solution were mixed with 14 c.c. of hydrochloric acid and diluted with water to 100 c.c. It was then heated to 70° by dipping the beaker in water of that temperature, and aqueous hydrogen sulphide was slowly added from a burette (the addition of 200 c.c. took 2½ hours), which at first gave rise to a turbidity, and then produced an orange coloured precipitate. Result:

Weight of dried precipitate	0·1823	gram.
" Sb_2S_3	0·1757	"
Composition of the precipitate	Sb_2S_3 =	77·17
	Sb_2S_5 =	22·83
		100·00

Experiment 22.—Experiment 21 was repeated at a temperature of 100°. The first drops of aqueous hydrogen sulphide produced, on the surface of the liquid, an orange coloured precipitate, which on stirring dissolved in the liquid and at the same time gave rise to a strong milky turbidity. Only after 15 c.c. of the reagent had been added (or after 9 minutes) was the first permanent, pale orange coloured precipitate obtained. It was treated very carefully to remove all sulphur. Result:

Weight of dried precipitate		0·1537 gram.
„ Sb_2S_3		0·1503 „
Composition of the precipitate....	Sb_2S_3 =	86·08
	Sb_2S_5 =	13·92
		100·00

Conclusion: With increase of temperature there is also an increase in the reduction and in the formation of antimony trisulphide.

It was now thought advisable to repeat Willm's experiments, namely, the action of hydrogen sulphide on antimonic solutions in the presence of tartaric acid, the reducing action of which Willm did not seem to suspect, any more than he did that of a high temperature.

Experiment 23.—50 c.c. of the above antimonic solution were diluted with 50 c.c. of water containing 1 gram of tartaric acid, heated to 70°, and precipitated by passing a rapid current of gaseous hydrogen sulphide. The liquid became milky at once, then, after 10 seconds, it acquired an orange colour, and after 25 seconds the first distinct precipitate was formed. After four hours (the passage of the gas was continued until the liquid became cold), the experiment was brought to an end. Result:

Weight of dried precipitate		0·0950 gram.
„ Sb_2S_3		0·0898 „
Composition of the precipitate......	Sb_2S_3 =	65·7
	Sb_2S_5 =	34·3
		100·0

The precipitate formed in this way, was considered by Willm to be pure, or approximately pure, antimony pentasulphide, whereas it consists of *two* parts of the trisulphide to *one* of the pentasulphide. The colour of such a mixture is always much lighter than that of the pure pentasulphide. Lastly, Willm states that such wet "pentasulphide" is *decomposed* into trisulphide and free sulphur, on washing with cold carbon bisulphide, a statement, the incorrectness of which is easily seen by comparing the Experiment 16 with Experiments 17—23, which show that the *pure* pentasulphide undergoes no such decomposition (Experiment 16) whereas under the conditions obtaining in Experiments 17—23 pure pentasulphide cannot be obtained.

The contrary statements of Rammelsberg (*Ann. Chem. Phys.*, 1874, **52**, 193), and of Braun (Michaelis, *Anorg. Chem.* V, Bd. II, p. 598) when compared with those of Bunsen and the results described in the present paper are easily explained by the incomplete state of oxidation of the antimony in the solutions used by the two first mentioned investigators.

Second Series of Experiments.

The object of this series was to study the above cardinal reaction in the presence of some foreign substances. The solutions used were those of metallic antimony in hydrochloric acid and potassium chlorate, and in order to complete the oxidation the necessary amount of a solution of potassium dichromate was added. The amount of the last reagent was smaller in the preparations called *A* and larger in preparations *B*. The precipitate was in each experiment washed with alcohol and carbon bisulphide, &c., and after being dried, as previously described, was finally converted into black antimony trisulphide.

Experiment 24.—10 c.c. of solution were mixed with 50 c.c. of water, 5 c.c. of hydrochloric acid added, and then 13 c.c. of a solution containing 0·0324 gram of potassium dichromate to complete the oxidation. A rapid current of hydrogen sulphide was passed in for half an hour. Result:

Weight of dried precipitate .... 0·1990 gram.
" Sb_2S_3 .... 0·1696 "
Composition of the precipitate...... $\left\{\begin{array}{l} Sb_2S_3 = 7{\cdot}64 \\ Sb_2S_5 = 92{\cdot}36 \end{array}\right.$
100·00

Experiment 25.—Same quantities as in Experiment 24, except that the hydrogen sulphide was passed in a very slow current.

Composition of the precipitate...... $\left\{\begin{array}{l} Sb_2S_3 = 8{\cdot}09 \\ Sb_2S_5 = 91{\cdot}91 \end{array}\right.$
100·00

Experiment 26.—10 c.c. of solution *B* were mixed with 50 c.c. of water, 5 c.c. of hydrochloric acid and 31 c.c. of a solution containing 0·0772 gram of potassium dichromate. It was precipitated with a rapid current of hydrogen sulphide. Result:

Weight of precipitate .... 0·2648 gram.
" Sb_2S_3 .... 0·226 "
Composition of precipitate.......... $\left\{\begin{array}{l} Sb_2S_3 = 8{\cdot}37 \\ Sb_2S_5 = 91{\cdot}63 \end{array}\right.$
100·00

Experiment 27.—Same conditions as in Experiment 26, except that the gas was passed in in a slow current. Result:

Weight of precipitate	0·2833 gram.	
„ Sb_2S_3	0·2428 „	
Composition of precipitate	Sb_2S_3 =	10·58
	Sb_2S_5 =	89·42
		100·00

Experiment 28.—The above solution and 25 c.c. of hydrochloric acid were used; the current of hydrogen sulphide was rapid.

Composition of precipitate	Sb_2S_3 =	26·06
	Sb_2S_5 =	73·94
		100·00

Conclusions: The reduction of antimonic acid is larger in the presence of chromic chloride than in its absence and increases as the amount of that salt present increases; it increases also with increase in the quantity of hydrochloric acid. The following experiments were made at a higher temperature.

Experiment 29.—10 c.c. of solution *B*, 15 c.c. of HCl, 31 c.c. of $K_2Cr_2O_7$, 50 c.c. of H_2O.

Slow current of H_2S was passed in at 50°. Result:

Weight of precipitate	0·1939 gram.	
„ Sb_2S_3	0·1885 „	
Composition of the precipitate	Sb_2S_3 =	82·58
	Sb_2S_5 =	17·42
		100·00

Experiment 30.—Same conditions as in Experiment 29, except that the hydrogen sulphide was passed into the solution heated at 70 . The solution became turbid, and an orange coloured precipitate was formed, which, after two hours, began to blacken, and became completely black when the gas was passed in at the said temperature for 10 hours. Result:

Weight of precipitate	0·1589 gram.	
„ Sb_2S_3	0·1559 „	
Composition of the precipitate	Sb_2S_3 =	88·21
	Sb_2S_5 =	11·79
		100·00

Experiment 31.—The precipitation took place at 100°. The orange coloured, amorphous precipitate formed was first converted into a distinctly crystalline, deep purple-red substance, with a violet tinge, which, after three hours, began to slacken, and became quite black after 10 hours. Result:

Weight of precipitate	0·1621 gram.
„ Sb_2S_3	0·1608 „
Composition	Sb_2S_3 = 94·89 Sb_2S_5 = 5·11
	100·00

On filtering off the above precipitate, the perfectly clear filtrate deposited an orange coloured precipitate on standing; this was probably antimony pentasulphide, 0·0023 gram of the precipitate giving 0 0019 gram Sb_2S_3 (Sb_2S_5 requires 0·00193 gram Sb_2S_3).

Experiment 32.—The conditions were the same as in Experiment 31; and the formation of the intermediate pink crystalline sulphide was also observed. Result:

Weight of precipitate................	0·1905 gram.
„ Sb_2S_3	0·1905 „

Composition of precipitate: Sb_2S_3 = 100·00 per cent.

Two problems presented themselves in the last series of experiments. The first was the appearance of the pink crystalline sulphide. Of the many attempts to isolate it, the following was not unsuccessful.

On passing the hydrogen sulphide at 50—55° into a solution which had required for its oxidation 31 c.c. of the above dichromate solution, a distinctly crystalline crimson-red or pink precipitate was obtained after eight hours. After removing all the free sulphur, it was dried at 106°, and gave 0·2070 gram of a substance which yielded 0·1886 gram of Sb_2S_3 (= 0·1347 Sb). Sulphur from the difference = 0·0723 gram.

The results agree perfectly with those required by the formula Sb_2S_4.

	Calculated.		Found.
2Sb	240	65·2	65·1
4S	128	34·8	34·9
	368	100·0	100·0

In all the other experiments made, heterogeneous precipitates were obtained, which were either orange, brown, or partly black, according to the time during which the hydrogen sulphide had acted. Their approximate composition was

Sb_2S_3	85
Sb_2S_5	15
	100

The second problem was the reducing action of the chromic salts.

Experiment 33.—25 c.c. of antimonic solution *A* was mixed with a solution of 1·2413 grams of crystallised chromic chloride in 25 c.c. of water, and after dilution with 50 c.c. of water a slow current of hydrogen sulphide was passed in for three hours. Result:

Weight of dried precipitate	0·1496 gram.
„ Sb_2S_3	0·1222 „
This corresponds Sb_2S_5	0·1455 „
Difference......	+0·0041 or + 2·74 p. c.

In spite of careful washing, 2·74 per cent. of sulphur more were produced and left in the precipitate above the limit either of Sb_2S_5 or $Sb_2S_3 + S_2$, although the greater part of the precipitate consisted of trisulphide and sulphur, which, however, could be only partly removed.

Experiment 34.—The same solution as that used in Experiment 33 was precipitated with hydrogen sulphide and washed with water only, after which it was dried.

Weight of precipitate obtained	0·16025 gram.
„ precipitate in Exp. 33	0·1496 „
Difference	0·01065 „

that is the amount of sulphur precipitated above the theoretical limit Sb_2S_5, which was soluble in, and had been removed by, carbon bisulphide.

Conclusions.

From the experiments described in this paper, the following conclusions may be drawn.

1. The total conversion of antimonious into antimonic compounds by the action of oxidising agents is a very difficult matter, requiring a large quantity of the oxidising agent and a lengthened period of action.

Such reagents as fuming nitric acid, potassium chlorate in hydrochloric solution, and even bromine in alkaline solution, except when the last acts for very many hours, do not produce complete oxidation.

2. When an excess of hydrogen sulphide—in the form of aqueous solution—acts *at once* on antimonic solutions at the ordinary temperature, pure *antimony pentasulphide* is formed; this shows that if Bunsen's directions are strictly followed, exact quantitative results can be obtained.

3. On acting with hydrogen sulphide on antimonic solutions under otherwise similar conditions:

a. The quantity of *antimony pentasulphide* increases:
  - *α.* The lower the temperature.
  - *β.* The more rapid the stream of hydrogen sulphide.

b. The quantity of *antimony trisulphide* mixed with sulphur increases:
  - *α.* The higher the temperature.
  - *β.* The slower the action of hydrogen sulphide.

4. As regards the dependence of the quantity of both sulphides on the amount of hydrochloric acid present, it appears that the quantity of the *pentasulphide* formed increases with that of the acid up to a certain maximum, lying between 10 and 20 per cent. of acid, after which limit it rapidly diminishes, with increase in the amount of hydrochloric acid.

5. In the presence of chromic salts, acid antimonic solutions are reduced by hydrogen sulphide more easily and more completely than when they are treated without such an addition.

6. Pure antimony trisulphide is obtained from antimonic solutions only in the presence of chromic salts; a slow current of hydrogen sulphide must be passed during a longer time at a higher temperature, and then the trisulphide is deposited in the black modification.

LVIII.—*Action of Hydrogen Sulphide on Solutions of Antimonic, Arsenic, and Telluric Acids.*

By Bohuslav Brauner, Ph.D., Professor in the Bohemian University, Prague, late Berkeley Fellow of Owens College.

The object of the present research is a comparative study of a definite reaction which takes place with analogous compounds of certain elements, having regard to the position of these elements in Mendeléeff's periodic system.

The action of hydrogen sulphide on arsenic acid was studied by Brauner and Tomíček (Trans., 1888, 53, 145), and shortly afterwards by Le Roy McKay.

An analogous work relating to antimonic acid has been done by Dr. Bošek, the results being given in the preceding paper. This work has naturally not exhausted the whole subject, but treating it from a somewhat empirical point of view has furnished material which may be taken as the basis of further experimenting and of a study of the mechanism of that reaction.

The following observation which I made many years ago formed the starting point of the work described in the preceding paper, and also of the present research.

A. *Action of Light on Antimony Pentasulphide.*

Antimony pentachloride was dissolved in hydrochloric acid and precipitated by the addition of 5 litres of an aqueous, saturated solution of hydrogen sulphide, subsequently passing a rapid current of gaseous hydrogen sulphide into the liquid; the orange coloured precipitate of antimony pentasulphide thus produced formed a layer several centimetres in thickness. The bottle containing the liquid and precipitate was placed in a window and exposed to full sunshine in the month of June, when it was observed that the precipitate became brown superficially, and after some time, black. It was then repeatedly shaken and exposed to the action of daylight or sunlight for about four years, when it was found to be so completely converted into a black, heavy crystalline powder, that only a few of the larger lumps showed traces of orange colour in the inside where the sunlight had no access. The volume of the original precipitate had diminished considerably.

This observation was made between the years 1887 and 1891, and the precipitate was analysed in order to see whether the black modification was trisulphide or pentasulphidene; a portion was dried, when it became grey, and on examination under the microscope it was seen that free sulphur was mixed with the black crystals.

Another part, after being well washed with water and alcohol, was repeatedly shaken with carbon bisulphide and again with alcohol, then dried and analysed.

0·4361 gave 0·3949 Sb_2O_4 = 0·3128 Sb. Sb = 28·51.
2·0412 „ 4·2384 $BaSO_4$ = 0·5821 S. S = 71·73.

	Calculated for Sb_2S_3.	Found.
Antimony	28·57	28·51
Sulphur	71·43	71·73
	100·00	100·24

The black crystals, therefore, are pure antimony trisulphide, the original substance being a mixture of sulphur with black *antimony trisulphide* (black modification discovered by Mitchell, Abstr., 1893, ii, 473, by boiling the red modification with dilute hydrochloric acid in a current of carbon dioxide).

The formation of this black trisulphide from the orange pentasulphide is due to a slow *photochemical decomposition* by the rays of the sun, thus: $(Sb_2S_5)_x + Aq = 2S_y + (Sb_2S_3)_z + Aq$. It was impossible to observe whether the less molecularly complex red trisulphide was formed first. It should be added that the long time taken for the completion of the above action was due to the fact that no less than 110 grams of antimony pentasulphide had been decomposed.

B. *Action of Heat on Antimony Pentasulphide.*

It is well-known that on heating dry antimony pentasulphide in a current of an inert gas at 210—220°, it decomposes leaving the black trisulphide, whilst sulphur escapes. It seems of interest to ascertain whether, under favourable conditions, a similar decomposition might not occur at a lower temperature in the presence of water.

For this purpose 1000 c.c. of water was acidified with 100 c.c. hydrochloric acid and 50 c.c. of a solution of potassium antimoniate containing 0·412 gram of Sb_2O_5 was poured in with continued stirring, so that a clear solution of antimonic acid was obtained. From this solution, pure antimony pentasulphide was precipitated by the addition of an excess of aqueous hydrogen sulphide. After pouring off one-half of the clear supernatant liquid, the other half containing the precipitate was treated with gaseous hydrogen sulphide. No change was observed to take place at the ordinary temperature. The mixture was then gradually heated to 85°, but after passing the gas for half a day the precipitate turned only slightly darker. It was then heated to 95° for half a day but no change took place.

On raising the temperature, however, to 97·5—99°, the liquid began to boil very slightly, and the precipitate turned dark brown, and finally black; at the end of three hours it was completely converted into a black, crystalline substance, a mixture of black antimony trisulphide and free sulphur. After the latter had been removed as completely as possible by repeatedly washing it with alcohol and carbon bisulphide, the residue was dried at 108°. On heating at 220 in a current of carbon dioxide 0·4380 gram lost only 0·0054 gram of free sulphur, but it is very probable that the last was contained in it as an "insoluble" modification formed by decomposition of hydrogen sulphide at a high temperature and in the presence of acids.

The percentage composition of the precipitate is therefore:—

	Found.	Calculated for Sb_2S_3.
Antimony	70·5	71·4
Sulphur	29·5	28·6
	100·0	100·0

from which it is seen that the analysed precipitate consisted almost entirely of black antimony trisulphide.

At 98° the following decomposition therefore takes place:

$$(Sb_2S_5)_x + Aq(+ HCl) = 2S_y + (Sb_2S_3)_z + Aq(+HCl),$$

and it is completely analogous to the decomposition by sunlight.

A similar formation of black antimony trisulphide was observed by Dr. Bošek in the presence of chromic chloride, and the question arose whether the last named substance does not promote the decomposition of the pentasulphide. The above experiment was repeated in the presence of chromic chloride, but I was surprised to find that, however vigorously the diluted or concentrated solution was boiled while a current of hydrogen sulphide was passed into it, no formation of black trisulphide took place.

C. *Catalytic Action of Chromic Chloride Solutions.*

If, however, as has been shown in the foregoing paper, chromic chloride is added first to the antimonic acid solution, and hydrogen sulphide is then passed in, a much stronger reduction of quiquevalent antimony to trivalent is observed than in the absence of the chromic salt and at the same time hydrogen sulphide is oxidised, and sulphur, partly in the "insoluble" form, separates.

A "catalytic" action takes place which is so far of interest as it is generally assumed that a solution of chromic chloride is not reduced by the action of hydrogen sulphide. I find, however, on passing hydrogen sulphide into a hot green solution of chromic chloride, that its colour becomes first violet and then of a deep blue, and strongly dichroitic. On working with the purest preparation, I find that some sulphur is always separated, so that a *slight* reduction to chromous salt may have taken place, although not a trace of a chromous compound could be detected in the liquid. I think that the "catalytic" action of chromic chloride may be explained by the following hypothesis.

In the hot liquid, chromic chloride is reduced, to a very slight extent indeed, to chromous chloride, thus:—

$$(a.)\ 2CrCl_3 + H_2S + Aq = 2CrCl_2 + 2HCl + S + Aq.$$

the chromous chloride reduces the antimonic to antimonious chloride;

$$(b.)\ 2CrCl_2 + SbCl_5 + Aq = 2CrCl_3 + SbCl_3 + Aq.$$

after which the reaction (*a*) takes place again and so on.

This hypothesis would also account for the formation of "insoluble" sulphur, as, according to Selmi, it is formed when hydrogen sulphide acts on ferric chloride:

$$2FeCl_3 + H_2S + Aq = 2FeCl_2 + S + 2HCl + Aq.$$

An analogous case was observed by Brauner and Tomíček on acting with hydrogen sulphide on a mixture of ferric chloride and arsenic acid.

D. *Analogy of Antimonic and Arsenic acids in their behaviour towards Hydrogen Sulphide.*

It is of some interest to compare the action of hydrogen sulphide on antimonic acid (Bošek) with that of hydrogen sulphide on arsenic acid (Brauner and Tomíček).

Arsenic and antimony are both members of the fifth group of Mendeléeff's system, the first belonging to the fifth series, the second to the seventh series. Antimony is therefore the next "atomic analogue" of arsenic.

During Bošek's work the question arose, What is the analogy and what the difference between the two elements when hydrogen sulphide acts on the aqueous acid solutions of their highest oxygen compounds?

Here a surprising analogy was observed, for both acids, under these circumstances, give either pure pentasulphide or a mixture of pentasulphide with the trisulphide and free sulphur, the following being the conditions.

Antimonic Acid.	*Arsenic Acid.*
(1.) More Sb_2S_5 is formed:	(1.) More As_2S_5 is formed:
(*a.*) The lower the temperature.	(*a.*) The lower the temperature.
(*b.*) The more rapid the current of H_2S.	(*b.*) The more rapid the current of H_2S.
(*c.*) The larger the quantity of HCl present (up to a certain limit).	(*c.*) The larger the quantity of HCl present (up to what limit?).
(2.) More Sb_2S_3 (and sulphur) is formed:	(2.) More As_2S_3 is formed:
(*a.*) The higher the temperature.	(*a.*) The higher the temperature.
(*b.*) The less rapid the current of H_2S.	(*b.*) The less rapid the current of H_2S.
(*c.*) The greater the difference from the limit of 10—20 p. c. HCl, upwards or downwards.	(*c.*) The less HCl present (the limit upwards has not been investigated).

It is seen that the analogy between arsenic and antimonic acids, so far as the question was studied (we do not know whether a large excess of hydrochloric acid present may not promote the formation of arsenic trisulphide) is as complete as possible, and it is *à priori* probable that the mechanism of the action may be the same. At the conclusion of the paper on arsenic acid, quoted above, I said it was impossible to explain as yet why a *small* quantity of hydrogen sulphide causes a formation of the *trisulphide*, whereas an excess produces only the *pentasulphide*, so that the question remains an interesting problem of chemical dynamics.

In 1888, Le Roy W. McKay threw considerable light upon that subject (*Amer. Chem. J.*, 1888, **10**, No. 6). He found that on adding a *small* quantity of hydrogen sulphide to a cold dilute acidified solution of an arsenate, some free *sulphoxyarsenic acid*, H_3AsO_3S, was formed thus,

$$1.\ H_3AsO_4 + H_2S = H_3AsO_3S + H_2O.$$

The *normal* reaction, which takes place between a solution of arsenic acid and a large excess of hydrogen sulphide is represented by the author thus,

$$2.\ 2H_3AsO_3S + 3H_2S = As_2S_5 + 6H_2O,$$

whereas the formation of a mixture of arsenic trisulphide and sulphur, which takes place in the presence of a small quantity of hydrogen sulphide, especially at a higher temperature, is a secondary one, and is represented by him thus,

$$(a)\ 2H_3AsO_3 + 6HCl = 2AsCl_3 + 6H_2O, \text{ and}$$
$$(b.)\ 2AsCl_3 + 3H_2S = As_2S_3 + 6HCl.$$

The question now arises: Is the great analogy shown, as regards the formation of either pentasulphide or a mixture of trisulphide and sulphur by both *arsenic* and *antimonic* solutions when treated with hydrogen sulphide, due to a strictly analogous chemical process?

Before trying to answer this question, we have to consider the well-known fact that when antimony is separated from arsenic by Bunsen's method (1878), in a solution containing both elements in the pentavalent state, the addition of hydrogen sulphide water causes the precipitation of antimony pentasulphide practically *at once*, whereas the arsenic acid remains practically completely in solution, while the excess of hydrogen sulphide is being driven out by a current of air.

After the liquid has been treated in the manner just described, Bunsen prescribes the addition of a few drops of chlorine water, undoubtedly with the object of oxidising some substance in solution. This substance may be either (*a*) arsenious acid, or (*b*) oxysulpharsenic acid, or (*c*) a small amount of hydrogen sulphide left in the liquid. As the question has never been discussed before, I may be allowed to say a few words about it.

Bunsen evidently intends to prevent the formation of any arsenic trisulphide by the subsequent action of the hydrogen sulphide.

Supposing (*c*) to be the aim, then, if a trace of hydrogen sulphide were left in the liquid—although this is highly improbable—it would certainly be destroyed.

As regards the oxidation of (*a*) arsenious acid, it is not very probable that it is formed during the process, and, if it were, that it would be entirely oxidised, as (*b*) the oxysulpharsenic acid undoubtedly present would also require chlorine for oxidation at the same time.

This last substance was unknown to Bunsen in 1877, and we have no available data regarding the amount or quantity in which it is formed during the process, but, if the few drops of chlorine water were supposed to destroy it entirely, its quantity must be very small.

In order to solve this question the following experiment was made.

E. *Action of Hydrogen Sulphide on Arsenic acid. Oxysulpharsenic acid.*

Five grams of arsenic trioxide was carefully and completely oxidised with nitric acid, the excess of the latter removed by evaporation, and the arsenic acid diluted with water to 1000 c.c.

Fifty c.c. containing 0·3589 gram of H_3AsO_4 was acidified with 10 c.c. of hydrochloric acid, and 200 c.c. of a freshly-saturated aqueous solution of hydrogen sulphide was added. Not a trace of a precipitate or turbidity was obtained. After stirring for several minutes, exactly as is done when antimony is to be separated from arsenic by Bunsen's method, a rapid current of filtered air was passed through the liquid contained in a covered beaker under a bell-jar, by suction (this plan besides being automatic, answers the purpose much better than the use of a foot-blower) for one hour in order to expel every trace of hydrogen sulphide, although 10 minutes would have been sufficient.

On adding a few drops of bromine water, separation of sulphur took place, showing that all the sulphoxyarsenic acid had not been destroyed, as it was only after the addition of about 10 c.c. of a strong solution of bromine in potassium bromide (Gladding solution: 50 c.c. Br, 75 grams KBr, 500 c.c. H_2O) that the sulphur present was entirely oxidised.

After removal of the excess of bromine, &c., the liquid yielded 0·2225 gram of barium sulphate, corresponding with 0·0306 gram of sulphur. This quantity represents 0·15074 gram of H_3AsO_3S, and as the arsenic acid present would have yielded 0·3991 gram of H_3AsO_3S, it is seen that 37·77 per cent. of the arsenic acid was converted into oxysulpharsenic acid. The sulphur found could only be from that compound, as 200 c.c. of the above hydrogen sulphide water when treated exactly in the same manner in a blank experiment (without any arsenic acid) gave no appreciable trace of barium sulphate.

The statement of McKay—"Sulphoxyarsenic is the end product, provided the amount of sulphuretted hydrogen which has acted on the arsenic acid is in comparison with the amount of arsenic acid in the dilute solution, *extremely small*"—requires alteration, for whereas the above quantity of arsenic acid requires 0·081 gram of sulphur for complete conversion into oxysulpharsenic acid, as much as 0·4 gram of sulphur was present in the hydrogen sulphide used; that is, five times the quantity required, and one-thirteenth of that was really absorbed.

I may be allowed to remark here that experiments made in this laboratory have shown that arsenious acid may be separated from arsenic acid quantitatively exactly as proposed by Bunsen for antimony and arsenic.

It is also of historical interest, and certainly does not diminish Bunsen's claims, to find the germ of his classical method in Gmelin's *Handbuch*, 5th edition (1853), **2**, 733.*

F. *Action of Hydrogen Sulphide on Antimonic acid.*

Whereas arsenic acid is converted first into oxysulpharsenic acid, even when hydrogen sulphide is in excess, antimonic acid is precipitated by this reagent almost instantly, and here lies a great difference between the two acids.

Further, not only is oxysulpharsenic acid known, but also its stable salts (Bouquet and Cloëz, McKay); whereas oxysulphantimonic acid has never been obtained, and all attempts to prepare the oxysulphantimonates have hitherto proved futile. I shall return to this subject hereafter.

These facts are, *à priori*, against a complete analogy as regards the mechanism of the action between hydrogen sulphide and arsenic acid on the one hand and antimonic acid on the other.

Before attempting to study the last question experimentally, we have to consider the difference in solubility of the two acids in water. The sparing solubility of antimonic acid in water is a function of the atomic weight of antimony, that is, the oxy-compounds of antimony, as a higher member of the fifth natural group are of a less negative (or more positive) character than those of the lower members of that group. On account of its sparing solubility, it is somewhat difficult, in the case of antimonic acid, to establish the same conditions of experimenting as McKay has done with arsenic acid.

Again it is not possible to obtain a slightly acidified solution of an antimoniate in the same way as it is with an arsenate, because in an aqueous solution of the relatively most soluble potassium antimoniate (the salt used in all subsequent experiments was that employed in qualitative analysis for the detection of sodium; its formula appears to me still somewhat doubtful), an insoluble precipitate of antimonic acid is produced on the addition of an acid. The only way in which a clear acid solution of antimonic acid could be obtained was by acidifying a large quantity of water with sulphuric or hydrochloric acid, and then pouring into it an aqueous solution of potassium antimoniate, stirring continuously. When too little mineral acid is used, a turbidity appears which cannot be easily removed.

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* Antimony is tested for arsenic thus: "Its powder deflagrated (verpufft) with about one-fourth part of saltpetre and treated with water, gives a filtrate containing potassium arsenate and antimoniate. It gives, therefore, on supersaturation with hydrochloric acid and then rapid saturation with gaseous hydrogen sulphide, a yellowish-red precipitate of *antimony pentasulphide;* after rapidly filtering and keeping in a closed vessel, a yellow precipitate of *arsenic pentasulphide* is obtained after a time." Unfortunately the author of this long forgotten method is not given. (The italics are mine.—B. B.)

For the following experiments, 15 grams of potassium antimoniate was dissolved in 1 litre of boiling water, and the cooled liquid filtered after a time. One hundred c.c. of the clear solution was found to contain a quantity of antimonic acid corresponding with 0·8236 gram of Sb_2O_5. This requires, for complete conversion into antimony pentasulphide, 220 c.c. of a freshly saturated solution of hydrogen sulphide containing about 0·2 gram of H_2S in 100 c.c.

Two thousand five hundred c.c. of water was strongly acidified with sulphuric acid and 100 c.c. of the above solution of potassium antimoniate was poured in, so that a clear solution was obtained. To this, 50 c.c. of hydrogen sulphide solution was added; an orange solution was produced, which, after some time, became opalescent. The hydrogen sulphide was so completely absorbed that its smell disappeared entirely after very short shaking of the closed flask. After a few hours, the opalescence changed to a turbidity, and at the end of 24 hours, a yellow precipitate separated of very nearly the same colour as the sulphides of arsenic.

In order to find whether it is not a compound corresponding to oxysulpharsenic acid, $Sb_2O_3S_2$, it was collected, repeatedly washed with a small quantity of water, and then successively with alcohol, with a mixture of alcohol and carbon bisulphide, with carbon bisulphide, and finally with alcohol. It was inferred by the turbidity of the filtrates that a large quantity of free sulphur was being washed out. After drying at 100°, it was analysed.

0·1164 gave 0·1035 Sb_2O_4. Sb = 70·20 per cent.
0·1885 „ 0·0222 $BaSO_4$. S = 1·62 „

From these data the calculated atomic proportion of sulphur to antimony is

$$S : Sb = 1 : 11{\cdot}6,$$

which shows that the compound is not the expected oxysulphide, in fact, that it is not a definite compound at all. The large quantity of free sulphur contained in it originally, that is sulphur from the hydrogen sulphide used for its precipitation, and amounting to 0·0941 gram, was almost entirely washed out by carbon bisulphide, and only 0·0049 gram of it was left in the precipitate as combined sulphur.

The following experiments were made with a hydrochloric solution of antimonic acid in order to avoid a possible admixture of sulphur from the sulphuric acid as used above.

Water, 2500 c.c., was acidified with 50 c.c. of hydrochloric acid, and 100 c.c. of the above antimoniate solution added; the clear solution was then mixed with 50 c.c. of hydrogen sulphide water. A deep orange solution was obtained, which in 15 minutes became opalescent and then turbid, and after 24 hours a yellow precipitate separated. This was collected, washed three times with a small quantity of water, then with alcohol and carbon bisulphide, dried, and analysed.

0·18125 gave 0·1679 Sb_2O_4. Sb = 73·15 per cent.
0·1228 „ 0·0068 $BaSO_4$. S = 0·76 „
0·1269 „ 0·0097 H_2O. H_2O = 7·64 „ (directly weighed after heating with anhydrous sodium carbonate in a current of air.) Total 81·55 per cent. As the precipitate contains nothing except mere traces of chlorine and potassium which were too small to be determined, the missing 18·45 per cent. were taken as oxygen. I call this Precipitate A.

Precipitate B was obtained exactly in the same way, but its free sulphur was *not* removed by washing with carbon bisulphide.

0·2823 gave 0·2071 Sb_2O_4. Sb = 57·92.
0·1761 „ 0·2144 $BaSO_4$. S = 16·73.
0·1666 „ 0·0163 H_2O by direct weighing. H_2O = 9·78.
Total 84·43 per cent. oxygen = 15·57 per cent.

In order to compare the composition of Precipitate A with that of B, the relation of combined sulphur to antimony was assumed to be the same in both precipitates, and, in addition to this, it was assumed that this sulphur was present in the form of antimony trisulphide. It does not alter the result much if it were present *partly* as pentasulphide. The percentage composition of the two precipitates is then—

	A	B.
Sb_2S_3	2·66	2·10
Free S	—	16·13
Sb_2O_3	50·05	31·00
Sb_2O_5	39·65	40 99
H_2O	7 64	9 78
	100·00	100·00

It is seen from the above very carefully conducted analyses (1) that the original precipitate is not an oxysulphide; (2) that it contains a considerable quantity of free sulphur; (3) that it contains some antimonic acid, together with its reduction product—antimonious acid. The two acids could not have been held completely in solution during the action but must have been carried down along with the small quantity of the sulphide (or oxysulphide?) precipitated, for it is noteworthy that the same solution, without the addition of hydrogen sulphide, remains clear for days.

Two atomic proportions of sulphur should give one molecular proportion of antimony trioxide, or $2S : Sb_2O_3 = 1 : 4{\cdot}5$, but the quantity of antimony trioxide found in the precipitate was really smaller, and so it was expected that some antimonious acid would be found in the original filtrates. This was proved to be the case by the following experiment.

The filtrate was precipitated with a large excess of aqueous sulphuretted hydrogen, the precipitate collected on a Gooch crucible, washed with carbon bisulphide, dried, and weighed. It was then converted into antimony trisulphide in a current of carbon dioxide at 220°, and weighed again. On multiplying the loss of weight (sulphur of the pentasulphide) by 6·2431, the quantity of pentasulphide is obtained. 0·4153 gram of the precipitate lost 0·0287 gram of sulphur. The percentage composition of the precipitate is

Sb_2S_3	56·86
Sb_2S_5	43·14
	100·00

This shows that more than half of the antimony contained in the filtrate is found in the state of antimonious acid.

In order to more fully study the action of hydrogen sulphide on an excess of antimonic acid, the following two series of experiments were made.

Series A.—Ten c.c. of the above standard solution of potassium antimoniate requires 22 c.c. of hydrogen sulphide water for complete precipitation; so less than half this quantity, namely 10 c.c., was used.

The solution of antimonic acid was prepared in each case by acidifying 100 c.c. of water with n c.c. of sulphuric acid of 25 per cent., and then adding 10 c.c. of antimoniate solution, and afterwards 10 c.c. of sulphuretted hydrogen water with the following results.

(A 1.) $n = 0$; solution perfectly clear and colourless; after some minutes, clear yellow, then an orange coloured turbidity. After 24 hours, only a trace of a precipitate is found at the bottom of the beaker. Hydrochloric acid gives a precipitate of antimony sulphide and the same precipitate is obtained on adding a solution of ammonium chloride.

If much water is added to the original solution, it turns orange, but will keep perfectly clear for a long time; sometimes it will not give any precipitate even on adding an acid and a large excess of hydrogen sulphide. Such a liquid must be assumed to contain the solution of a colloïdal form of antimony pentasulphide, probably free sulphantimonic acid.

(A 2.) $n = 0{\cdot}05$ c.c.; orange coloration at once; after one minute, a slight opalescence; no turbidity after one hour; at the end of 24 hours, a pale yellow turbidity.

(A 3.) $n = 0{\cdot}1$ c.c.; same as (A 2), the liquid becomes turbid, and after 24 hours a trace of a white precipitate separates from the orange solution.

(A 4.) $n = 0{\cdot}2$ c.c.; same as (A 3); no precipitate. After one hour, an orange precipitate begins to form; and, after 24 hours, another layer of a yellow precipitate is deposited upon the first. The supernatant liquid is colourless and slightly turbid.

(A 5.) $n = 0{\cdot}5$ c.c.; same as (A 4). Light orange precipitate after one hour, but the solution keeps clear the longest of the whole series. Later on, a paler precipitate separates, and the liquid becomes orange coloured and very turbid. After 24 hours the upper precipitate is pure yellow, and the supernatant liquid clear and colourless.

(A 6.) $n = 1$ c.c.; orange turbidity at once; after shaking, a copious precipitate of the colour of antimony pentasulphide separates, and later on there is a precipitate of the colour of arsenic trisulphide. The supernatant liquid is colourless and slightly turbid, but from this. after 24 hours, a yellowish-white precipitate separates, and the liquid becomes perfectly clear.

(A 7.) $n = 2$ c.c.; turbidity at once, and, after shaking, a copious orange precipitate; liquid almost clear.

(A 8.) $n = 4$ c.c.; same as (A 7).

(A 9.) $n = 8$ c.c.; same as (A 8).

(A 10.) $n = 16$ c.c.; same as (A 9).

(A 11.) $n = 32$ c.c.; same as (A 10); liquid clear.

Series B. The conditions were the same as in A except that only half the volume of H_2S-water, that is, 5 c.c. was added.

(B 1.) $n = 0$; solution clear and colourless; after 24 hours, an orange opalescent turbidity, but no precipitate.

(B 2.) $n = 0{\cdot}05$ c.c.; pale yellow, clear solution, becoming opalescent; after one hour, a strong yellow opalescence; after 24 hours, a pale yellow turbidity, but no precipitate.

(B 3.) $n = 0{\cdot}1$ c.c.; clear yellow solution; after one hour, strong white opalescence; after 24 hours, a pure white precipitate separated from the clear, colourless liquid. According to an analysis, the white precipitate contains free sulphur, together with antimonious and antimonic acids, but absolutely no sulphur is combined with antimony.

(B 4.) n = 0·2 c.c., darker yellow solution, then opalescence. After one hour, strong, white opalescence; after 24 hours, a white precipitate. When more acid is present than in B 3 and B 4, some antimony will be separated as sulphide, and this increases with the quantity of free acid present.

(B 5.) n = 0·5 c.c., clear yellow solution, which keeps transparent the longest of the whole series. After one hour, a strong, yellowish-white opalescence; after 24 hours, a nearly white precipitate with a slight, sulphur-yellow shade.

(B 6.) n = 1·0 c.c., solution clear yellow, soon becomes turbid. After one hour, a precipitate of the colour of arsenic trisulphide, liquid same turbidity; after 24 hours, a yellow precipitate.

(B 7.) n = 2 c.c., solution at once turbid. After 24 hours, a yellow precipitate with a white layer over it.

(B 8.) n = 4 c.c.; same as B 7.

(B 9.) n = 8 c.c.; same as B 8.

(B 10.) n = 16 c.c.; same as B 9.

(B 11.) n = 32 c.c., yellow turbidity. After one hour, pale orange flocks; liquid clear. No change after 24 hours.

After this, some of the precipitates obtained in a similar way were analysed.

To 2000 c.c. of water, 5 c.c. HCl, 100 c.c. of antimoniate solution, and 50 c.c. of H_2S water were added. A clear, yellow precipitate separated; this was washed with dilute hydrochloric acid and kept long in contact with an excess of hydrogen sulphide water, in order to convert free antimonious and antimonic acid into the sulphides. After washing with water, carbon bisulphide, &c., it was found to consist of

Sb_2S_5	43·5
Sb_2S_3	56·5
	100·0

The precipitate corresponding to (B 11) was prepared next by mixing 1000 c.c. H_2O, 320 c.c. H_2SO_4, 100 c.c. of antimoniate solution, and 50 c.c. H_2S water. An orange coloured precipitate separated *at once*.

On washing with carbon bisulphide, it evidently lost much free sulphur. It contained

Sb_2S_5	59·95
Sb_2S_3	40·05
	100·00

G. *Hypothetical Potassium Oxysulphantimoniate.*

The precipitate corresponding to (B 1) was prepared by mixing 100 c.c. of antimoniate solution and 50 c.c. of hydrogen sulphide water. The solution soon became yellow, and then a pale orange opalescence was produced; on adding a saturated solution of ammonium chloride, an orange precipitate was formed. Half of the precipitate was analysed after filtration and washing with water only (A), the other half after washing with carbon bisulphide, when it was found to lose free sulphur (B); this precipitate is deep red.

A. 0·209 gram yielded 0·1698 gram Sb_2S_3. The precipitate contains therefore, for every 100 parts of Sb_2S_3, 23·09 parts of sulphur, free and combined.

B. 0·1564 gram yielded 0·1440 gram Sb_2S_3. The precipitate contains for every 100 parts of Sb_2S_3, 8·60 parts of combined sulphur.

From the above data the composition of the precipitate is calculated.

Antimony trisulphide	44·56
Antimony pentasulphide........	43·67
Free sulphur..................	11·77
	100·00

The composition of this precipitate, after the removal of free sulphur, corresponds very closely with that of antimony tetrasulphide.

In the experiments A 1 and B 1, and in that just described, salts of oxysulphantimonic acid ought to have been formed if they are capable of existence.* In fact the solution originally obtained is colourless, and it is possible that it contains potassium oxysulphantimoniate, $K_3SbO_4 + H_2S + Aq = K_3SbO_3S + H_2O + Aq$ (this equation being, of course, hypothetical†). This salt, however, is very unstable and decomposes very soon. The colourless liquid becomes yellow, then orange, and opalescent as described under A_1 and B_1; on adding ammonium chloride, a mixture of antimony pentasulphide and trisulphide with free sulphur is separated.

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* Feit and Kubierschky (*Ber.*, 1888, 21, 1660) have made a series of experiments with the object of preparing oxygen derivatives of sulphantimonic acid (oxysulphantimoniates, &c.). The results obtained were entirely negative, and the authors conclude from their experiments that derivatives of antimonic acid containing less than four atoms of oxygen replaced by sulphur are incapable of existence at the ordinary temperature. Their experiments are, however, not identical with those made above.

† Assuming that antimonic acid is a monobasic acid, the formulæ of it and of its derivatives in the above, and in the equations which occur later on, would become

It should be added that this liquid containing, hypothetically, potassium oxysulphantimoniate, immediately after the hydrogen sulphide solution has been added, has the odour of that gas, and that, even if the quantity of the latter is insufficient to convert all the antimony into sulphide; silver sulphate also produces in it a black precipitate of silver sulphide. After several hours, however, when absorption of the hydrogen sulphide is complete, the liquid is yellow or orange, and decomposition has taken place. The solution with silver sulphate now gives a greyish-brown precipitate which after some time turns black.

A neutral solution of potassium antimoniate gives, with silver sulphate, a white precipitate; but a strongly acid solution, obtained by adding antimoniate solution to dilute sulphuric acid, is not precipitated by silver sulphate, although if silver sulphate or silver sulphantimoniate is precipitated from such a solution, the precipitate is invariably white. For this reason it was very difficult to repeat with such solutions McKay's reactions of oxysulpharsenates. When, however, an excess of hydrogen sulphide is added to a neutral solution of potassium antimoniate, decomposition occurs in a very short time with strong orange-coloured turbidity, followed by separation of an orange-coloured precipitate.

The above and this last mode of decomposition of a solution of the hypothetical oxysulphantimoniate of potassium is, however, perfectly analogous to the decomposition of potassium oxysulpharsenate during its formation. McKay has observed that on treating a hot solution of potassium arsenate with a rapid current of hydrogen sulphide, "a considerable amount of sulphide of arsenic" (trisulphide or pentasulphide? B. B.) "separates out." With potassium antimoniate, the same decomposition was observed by me to take place in the cold.

The study of this peculiar decomposition would be an interesting subject for further research. I am not quite satisfied with the results obtained, so as to be able to express the mode of decomposition of this hypothetical solution of potassium oxysulphantimoniate by means of an equation, and other work which I regard as more important does not allow me to devote more time to it.

$HSbO_3$, $KSbO_3$, $HSbS_3$, $HSbO_2S$, instead of
H_3SbO_4, K_3SbO_4, H_3SbS_4, H_3SbO_3S,

but this change is of no cardinal importance as regards the final conclusions arrived at.

H. *Hypothetical Sulphantimonic and Oxysulphantimonic acids.*

It has been shown above that on acting on a solution of antimonic acid with an insufficient quantity of hydrogen sulphide, reduction to antimonious acid, accompanied by the separation of free sulphur, takes place after several hours.

Let us first consider the question whether this action could be explained by the "old reduction hypothesis."

$$H_3SbO_4 + H_2S + Aq = H_3SbO_3 + H_2O + S + Aq.$$

This hypothesis is disproved by the following observations.

1. On adding to an acid solution of an antimoniate a quantity of hydrogen sulphide insufficient for complete precipitation of the antimony as pentasulphide, an orange, opalescent liquid is obtained. Hydrogen sulphide is so quickly and completely absorbed that the liquid smells of it only for a few seconds, and gives with silver nitrate or sulphate a black precipitate of silver sulphide. Immediately afterwards the atmosphere of the vessel is without action on lead paper, and silver sulphate produces only a light brown precipitate, which after many hours decomposes and becomes black. On account of the instability of the silver precipitate and of the solution, it was impossible to repeat with the latter McKay's reactions for oxysulpharsenic acid. It is, however, seen that hydrogen sulphide as such does not reduce antimonic acid, and that its sulphur is completely combined with antimony, most probably as sulphantimonic acid.

2. Very few experiments have been published from which we can judge as to whether antimonic acid is reduced easily or with difficulty by reducing agents. In order to answer this question, sulphurous acid in large excess was added to a solution of potassium antimoniate in sulphuric acid, and after it had been allowed to act for 24 hours, the excess was completely removed by a rapid current of air.

The liquid, from which some antimonious hydroxide had separated, was then strongly acidified with hydrochloric acid and precipitated with a large excess of aqueous hydrogen sulphide. The precipitate was collected, washed with carbon bisulphide, dried first at 105°, and then at 220° in carbon dioxide.

0·3125 gave 0·2999 Sb_2S_3, so that the composition of the precipitate is

Antimony trisulphide..........	74·83
Antimony pentasulphide	25·17
	100·00

This experiment disproves the reduction hypothesis, for it shows that such a powerful reducing agent as sulphurous acid, even when present in large excess and acting for a long time, is unable to reduce more than three-quarters of the antimonic acid present to antimonious acid, and thus a direct reduction by hydrogen sulphide becomes very improbable, especially as its sulphur combines directly with antimony.

Whatever the proportion between antimonic acid, free mineral acid, and hydrogen sulphide, it is always found that the sulphur of the hydrogen sulphide enters first into combination with antimony. The sulphide exists at first in a colloïdal state in solution, so that the latter may be assumed to contain the hypothetical sulphantimonic acid H_3SbS_4.

Now we have the following alternatives.

1.—When hydrogen sulphide is present in excess, together with a free mineral acid, the sulphantimonic acid produced at first is decomposed with formation of pure antimony pentasulphide.

$$(a.)\ 2H_3SbO_4 + 8H_2S + Aq = 2H_3SbS_4 + 8H_2O.$$

$$(b.)\ 2H_3SbS_4 + n\mathrm{HCl} + Aq = Sb_2S_5 + 3H_2S + n\mathrm{HCl}.$$

Here we have a cardinal difference between antimony and arsenic, for whereas arsenic acid is not precipitated by hydrogen sulphide until after the lapse of some time, a soluble form of antimony sulphide is produced at once in a solution of antimonic acid, as seen from the deep orange colour of the liquid. In this respect, antimonic acid resembles arsenious acid, or behaves very like the other more positive compounds of the metals of the hydrogen sulphide group.

2.—In the second alternative the antimonic acid is in excess over the quantity of hydrogen sulphide. On considering all the experiments contained in the present and the foregoing paper, the following explanation appears to me to be the most probable.

At first some sulphantimonic acid is also formed, but this, in contact with the excess of free antimonic acid present, combines to form oxysulphantimonic acid, thus

$$(a.)\ H_3SbS_4 + 3H_3SbO_4 + Aq = 4H_3SbO_3S + Aq.$$

This must be a very unstable compound which, as soon as it is formed, decomposes into antimonious acid and free sulphur, thus

$$(b.)\ nH_3SbO_3S + m\mathrm{HCl} + Aq = nH_3SbO_3 + nS + m\mathrm{HCl} + Aq.$$

The deep orange colour of the liquid first formed, and corresponding to the state (*a*), disappears more or less completely on standing, and antimonious acid is formed, together with free sulphur, corresponding with the state (*b*).

This ideal case, corresponding with the decomposition of McKay's oxysulpharsenic acid at a higher temperature, was reached in the experiments (B 3) and (B 4), when a pure white precipitate, a mixture of free sulphur with antimonious acid, alone separated. It depends also on the proportion of free acid present whether antimonious acid remains in solution or whether it is partly precipitated.

In the majority of cases described in this and the foregoing paper, the reaction 2 is accompanied by the reaction 1, for, as seen from the experiments (A 4—11) and (B 5—11), the presence of more free acid, *cœteris paribus*, causes the decomposition of a part of the sulphantimonic acid first formed, the antimony pentasulphide being precipitated instead of entering into unstable combination with antimonic acid. In addition to this, the action is complicated in so far as some antimony trisulphide is thrown down along with the pentasulphide, the trisulphide being formed most probably by the direct action of hydrogen sulphide on antimonious acid formed rapidly in the mode 2(*b*) when a large excess of free mineral acid is present. (See analysis corresponding with experiment B 11.)

That considerable time is required before the state of unstable equilibrium corresponding with the formation of oxysulphantimonic acid is reached is seen from Dr. Bošek's experiments 18 and 19 (this vol., p. 520), when the addition of hydrogen sulphide solution, even drop by drop, was too rapid to cause a reduction of more than 3—5 per cent. in two hours. It is unfortunate that the formation of *insoluble* sulphur, which takes place in the presence of a larger quantity of hydrochloric acid (experiment 20), complicates the phenomenon, as the presence of a large quantity of free mineral acid evidently promotes the rate of formation of oxysulphantimonic acid.

When working at a higher temperature, oxysulphantimonic acid is formed more rapidly, and reduction reaches 77 per cent. at 70° (experiment 21), whereas at 100° as much as 86 per cent. of antimony trisulphide is formed. Here the analogy to oxysulpharsenic acid is far more apparent, although, under the same conditions, the formation of arsenic trisulphide will undoubtedly reach a still higher percentage.

In all the reactions described, the more positive character of antimony as compared with arsenic appears distinctly, and this difference between the two elements corresponds exactly with their position in the periodic system, especially with that of antimony, as being a higher member of the fifth group than arsenic.

Antimony forms a transition to the highest, most positive member of the same group, namely, bismuth, the pentavalent oxygen compound of which—a peroxide of the water type—oxidises hydrogen sulphide merely, and does not form a pentasulphide. The behaviour of its tervalent compounds towards hydrogen sulphide brings it among the more positive metals of the mercury, lead, &c., group.

I. *Action of Hydrogen Sulphide on Telluric acid.*

The third analogous acid, the behaviour of which towards hydrogen sulphide has been investigated, is telluric acid. It is more negative than antimonic acid, owing to the position of tellurium in the same (seventh) series as antimony, and in its immediate neighbourhood in the sixth group. It forms a transition to periodic acid, which is so negative that it is not precipitated by hydrogen sulphide.

From the many experiments made by me with the object of studying telluric acid, and especially its behaviour towards hydrogen sulphide, only those are here of interest which show its analogy to or difference from arsenic and antimonic acids.

The behaviour of hydrogen sulphide towards telluric acid is closely analogous to its action on arsenic acid, not only in that its cold dilute aqueous solution, pure or acidified, is not at once precipitated by hydrogen sulphide, but also that a very long time elapses before precipitation takes place.

Brauner and Tomiček have shown that when an excess of hydrogen sulphide in the gaseous form acts at the ordinary temperature on a solution of arsenic acid, 97·83 to 99·37 per cent. is precipitated as sulphide after 24 hours, and 99·87 per cent. after 48 hours (Trans., 1888, 53, 147, 148, 151). McKay has proved that in a closely stoppered bottle complete precipitation takes place in two weeks.

Telluric acid treated in exactly the same way, that is, when an acid solution is put into a closely stoppered bottle with an excess of aqueous hydrogen sulphide, gives the first trace of a turbidity after the lapse of 24 hours, the first trace of a precipitate after two or three days, and even after being kept in the dark and cold for more than two months only a very small percentage is precipitated.

In order to find whether any sulphoxytelluric acid is formed in the cold, 0·2831 gram of crystallised telluric acid was dissolved in 50 c.c. of water, 10 c.c. of hydrochloric acid added, and then 200 c.c. of freshly prepared hydrogen sulphide solution. The liquid, from which nothing had been precipitated by hydrogen sulphide, was freed from the excess of this reagent by a current of air, after which it was oxidised in exactly the same manner as described under E. But whereas in the case of arsenic acid 37·77 per cent. of the latter was converted into oxysulpharsenic acid, not a trace of combined sulphur was found in the liquid in the case of telluric acid, proving that not a trace of sulphoxytelluric (oxysulphotelluric) acid was formed under the same conditions.

The excess of hydrogen sulphide was removed, after the lapse of two days, from a mixture of 0·14 gram of telluric acid with 0·25 gram of sulphuric acid and 60 c.c. of hydrogen sulphide solution. The liquid was tested for sulphoxytelluric acid with silver sulphate solution, but not a trace of a precipitate was obtained in the acid or in the nearly neutralised solution.

In order to precipitate a solution of telluric acid completely by excess of hydrogen sulphide, the closed vessel containing the mixture must be heated in boiling water for six to eight hours at least, so difficult is it to precipitate telluric acid completely.

0·270 gram of pure crystallised telluric acid, H_6TeO_6 (which is very difficult to prepare), after complete precipitation with hydrogen sulphide in a closed vessel and drying in a current of carbon dioxide for two hours at 100°, gave 0·2641 gram of a mixture of tellurium and sulphur corresponding with the atomic proportion of $Te + S_3$ (the quantity calculated is 0·2632 gram). On heating at 230° in a current of carbon dioxide until the weight became constant, 0·1524 gram of tellurium was left (calculated 0·1501 gram).

0·270 gram of telluric acid, precipitated in the same way with hydrogen sulphide, gave 0·1534 gram after washing with carbon bisulphide and drying for two hours in a current of carbon dioxide at 100°. This residue is evidently a mixture of nearly pure tellurium with a trace of sulphur only, for on heating in carbon dioxide at 230° for three hours it yielded 0·1528 gram of residue.

These two experiments prove (1) that the precipitation is complete under the conditions described; (2) that the precipitate consists essentially of a mixture of tellurium and free sulphur in the atomic proportion $Te + S_3$; (3) that from this mixture sulphur may be removed either by washing with carbon bisulphide or by heating at 230° in an inert gas. If any sulphur is *combined* with tellurium, its quantity is exceedingly small. These observations are of some interest with regard to the quantitative analysis and determination of telluric acid.

The following experiments were made in order to see whether any reduction takes place when hydrogen sulphide acts on telluric acid, the latter being in excess.

0·270 gram of telluric acid was dissolved in 150 c.c. of freshly boiled water and 30 c.c. of freshly prepared hydrogen sulphide solution was added, an amount sufficient to precipitate only one-half of the telluric acid present; the tightly closed flask containing the mixture was then heated in boiling water for two hours. As no mineral acid was added, a black liquid was obtained containing a solution of a colloïdal modification of tellurium together with sulphur. In order to obtain a precipitate which could be filtered off, the flask was opened for a moment, and 1 c.c. of sulphuric acid of 25 per cent. added, when it was perceived that the smell of hydrogen sulphide had not yet completely disappeared. The flask was then heated for two hours more at 100°, after which the hydrogen sulphide was found to be completely absorbed; the precipitate was collected in a Gooch crucible and dried for three hours at 100—102° in carbon dioxide; it weighed 0·1272 gram. It was then heated in the same gas for two hours at 230°, when it was found to weigh 0·0707 gram. The precipitate consisted, therefore, of 0·0707 gram of tellurium and 0·0565 gram of sulphur. According to the two foregoing experiments, the weight of the sulphur ought to have been 0·0517 gram, but, as calculated from the amount of hydrogen sulphide used, it should be 0·0565 gram—the weight really found. The excess of 0 0048 gram is therefore due to reduction.

It has hitherto been impossible to detect any trace of a sulphoxytelluric acid in the filtrate.

The following experiment, analogous to Rose's experiment with arsenic acid, was made:—0·270 gram of telluric acid was dissolved in water, some sulphuric acid added, then hydrogen sulphide solution in excess, and the whole heated in an open beaker rapidly to boiling, until the excess of hydrogen sulphide was expelled. A small, very pale brown precipitate was formed which consisted of a very small quantity of tellurium together with a comparatively larger amount of sulphur. Here, evidently, reduction had taken place. This was proved by filtering off the precipitate and adding to the clear, colourless filtrate some hydrogen sulphide solution; a brown coloration was immediately produced, proving that the filtrate contained a small quantity of *tellurous* acid. No trace of sulphoxytelluric acid could be found in the filtrate, so that, if it was formed, it must have been destroyed by boiling.

It should be noted that no sulphoxytellurates have hitherto been obtained, and that, therefore, judging from the analogy to antimony, sulphoxytelluric acid will be a very unstable substance. Its formation in the cold could not be observed, whereas if it were formed at a higher temperature it must have been immediately destroyed.

In order to test the "old reduction hypothesis," telluric acid was subjected to the action of sulphurous acid.

0·270 gram was dissolved in water and heated with 200 c.c. of aqueous sulphurous acid in a closed vessel for five hours; the precipitated tellurium was collected on a Gooch filter, washed and dried in carbon dioxide at 100°; its weight was 0·0167 gram, or only about one-tenth of the total quantity (0·1526 gram) which is contained in the acid taken.

This proves how extremely difficult it is to reduce telluric acid even by such a powerful reducing agent as sulphurous acid, and, for the same reasons as given in the analogous experiment made with antimonic acid, I conclude that the reduction hypothesis, $H_2TeO_4 + H_2S + Aq = H_2TeO_3 + S + H_2O + Aq$, is equally disproved.

Conclusions.

Summarising the results of the experiments made with arsenic acid, antimonic acid, and telluric acid, it is seen that, as regards the property of not being immediately precipitated by hydrogen sulphide, telluric acid resembles arsenic acid, but it surpasses it in so far as it is acted on by that reagent with far greater difficulty. It is also far more difficult to reduce by sulphurous acid.

It differs from arsenic acid in so far as no sulphoxytelluric acid is formed in the cold.

It resembles antimonic acid in the arrangement of atoms corresponding with the formation of a sulphoxytelluric acid being very unstable, but it differs from it in that if the acid in question is formed at a high temperature it is immediately destroyed.

Tellurium differs, however, most essentially both from arsenic and from antimony, in the fact that tellurous acid as well as telluric acid when precipitated with hydrogen sulphide, give, as a final product of the action, precipitates consisting almost entirely of free tellurium and of free sulphur in the atomic proportions $Te + S_2$ or $Te + S_3$. It is therefore impossible to investigate the question whether telluric acid when treated with hydrogen sulphide, under certain conditions, gives the bisulphide, and under other conditions the trisulphide, in the same way as this could be done with arsenic and antimony, for their sulphides are relatively stable.

The higher member of the sixth group, fifth series, selenic acid is not acted on by hydrogen sulphide at all in aqueous solution. The still higher member of the sixth group, third series, sulphuric acid is reduced by hydrogen sulphide directly: $H_2SO_4 + H_2S = SO_2 + S + 2H_2O$ (in the absence of water).

The difference in behaviour of the acids in question is in complete accordance with what might be expected from the position of the corresponding elements in the periodic system.

cent. added, when it was perceived that the smell of hydrogen sulphide had not yet completely disappeared. The flask was then heated for two hours more at 100°, after which the hydrogen sulphide was found to be completely absorbed; the precipitate was collected in a Gooch crucible and dried for three hours at 100—102° in carbon dioxide; it weighed 0·1272 gram. It was then heated in the same gas for two hours at 230°, when it was found to weigh 0·0707 gram. The precipitate consisted, therefore, of 0·0707 gram of tellurium and 0·0565 gram of sulphur. According to the two foregoing experiments, the weight of the sulphur ought to have been 0 0517 gram, but, as calculated from the amount of hydrogen sulphide used, it should be 0·0565 gram—the weight really found. The excess of 0·0048 gram is therefore due to reduction.

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This proves how extremely difficult it is to reduce telluric acid even by such a powerful reducing agent as sulphurous acid, and, for the same reasons as given in the analogous experiment made with antimonic acid, I conclude that the reduction hypothesis, $H_2TeO_4 + H_2S + Aq = H_2TeO_3 + S + H_2O + Aq$, is equally disproved.

Conclusions.

Summarising the results of the experiments made with arsenic acid, antimonic acid, and telluric acid, it is seen that, as regards the property of not being immediately precipitated by hydrogen sulphide, telluric acid resembles arsenic acid, but it surpasses it in so far as it is acted on by that reagent with far greater difficulty. It is also far more difficult to reduce by sulphurous acid.

It differs from arsenic acid in so far as no sulphoxytelluric acid is formed in the cold.

It resembles antimonic acid in the arrangement of atoms corresponding with the formation of a sulphoxytelluric acid being very unstable, but it differs from it in that if the acid in question is formed at a high temperature it is immediately destroyed.

Tellurium differs, however, most essentially both from arsenic and from antimony, in the fact that tellurous acid as well as telluric acid when precipitated with hydrogen sulphide, give, as a final product of the action, precipitates consisting almost entirely of free tellurium and of free sulphur in the atomic proportions $Te + S_2$ or $Te + S_3$. It is therefore impossible to investigate the question whether telluric acid when treated with hydrogen sulphide, under certain conditions, gives the bisulphide, and under other conditions the trisulphide, in the same way as this could be done with arsenic and antimony, for their sulphides are relatively stable.

The higher member of the sixth group, fifth series, selenic acid is not acted on by hydrogen sulphide at all in aqueous solution. The still higher member of the sixth group, third series, sulphuric acid is reduced by hydrogen sulphide directly: $H_2SO_4 + H_2S = SO_2 + S + 2H_2O$ (in the absence of water).

The difference in behaviour of the acids in question is in complete accordance with what might be expected from the position of the corresponding elements in the periodic system.

LIX.—*On the Atomic Weight of Tellurium.*

By Bohuslav Brauner, Ph.D., Prague.

Having been engaged since 1883 in investigating tellurium, especially with the object of determining its atomic weight, I desire briefly to call attention to the position in which the problem now stands, and to place on record certain conclusions to which I have been led, as they are of a somewhat novel character and of interest in connection with the recent discovery of argon.

My analyses of tellurium tetrabromide—of which I presented a full account to the Society in 1889 (Trans., **55**, 381—411)—gave the value, Te = 127·64, as referred to the standard atomic weights, O = 16, Ag = 107·93, Br = 79·95, or, on reduction to a vacuum, Te = 127·71, instead of 125, the number generally accepted. As this is 0·86 higher than the atomic weight of iodine, 126·85, whereas from the position of tellurium in the periodic series, the atomic weight assignable to it should be 123—125, I was led to the conclusion that tellurium as described is not a simple substance; and in the paper in question I drew attention to facts which appeared to support this view.

Through the kindness of Dr. Ludwig Mond, to whom I would here give my best thanks, I have since been enabled to work with considerable quantities of tellurium preparations. A large quantity of tellurium which was purified by the method described in my paper (*loc. cit.*), but not distilled, appeared to be free from all ordinary impurities—even when examined spectroscopically—and might have been regarded as chemically pure; but on converting it into sodium sulphotellurate and subjecting this to a series of fractional precipitations, fractions of the dioxide were obtained which when analysed by titration with N/10 permanganate (see Trans., 1891, **59**, 58—67; 238—253) gave results showing a variation in the equivalent.

On subjecting the extreme fractions to the minutest examination, it was found that the following known elements could be separated from them: at the positive end mercury, thallium, bismuth, copper, lead; at the negative, arsenic and antimony. The intermediate fraction, after being further purified and converted into tellurium dioxide, on titration with permanganate, gave numbers varying only very slightly.

I at first thought that I should succeed in splitting up tellurium into the true tellurium (Te = 123—125) and Mendeléeff's hitherto unknown Dwitellurium (Dwt = 214), but from a careful study of the subject, and especially of telluric acid, I conclude that it is very improbable that the abnormally high "atomic weight" of tellurium is due to an admixture of a higher homologue of tellurium, having the atomic weight 214.

I have spent a great deal of time in carefully studying telluric acid, and find that it is extremely difficult to obtain it in a pure state; this was done with the object of determining the atomic weight of tellurium by its analysis as a check on the value deduced from the examination of the tetrabromide. One "ratio" confirms that value; but on trying to obtain other atomic ratios, telluric acid is found to behave as a mixture of two substances. I may here add that I have discovered a new modification of telluric acid, the existence of which was predicted by Berzelius; it corresponds with the yellow tellurates, whereas the ordinary acid corresponds with the white tellurates.

As there can be little doubt that tellurium has an "atomic or combining weight" of 127·7, several chemists have proposed to place it in the VIIIth group of Mendeléeff's system. The most important reasons are those given by Retgers (*Zeit. physikal. Chem.*, 1891, 8, 6—75). From the study of the crystalline forms of sulphur and tellurium and their compounds, he is inclined to consider that the two elements are not isomorphous; whereas if tellurium is placed in the VIIIth group, it exhibits certain properties in common with ruthenium and osmium. Quite apart from the fact that there is no law that all elements of a natural group must be isomorphous, I do not agree with this view of Retgers, for although tellurium has hitherto been regarded as the highest member of the natural group, O S Se Te, yet since the discovery of Argon by Lord Rayleigh, and Dr. Ramsay, the question has assumed a perfectly new aspect, and I have little doubt—supposing that Dewar's view, defended by Mendeléeff, Berthelot, the author of this paper and others, according to which Argon is allotropic nitrogen, N_3 (which became very probable after the discovery of Helium, H_3 or H_4), should prove erroneous—that Argon must be regarded as an element or a mixture of elements belonging to a new group in the periodic system, namely the VIIIth group of the *typical elements* and of the elements of the *odd series*.

VIIIth group. $A^1 = 20$. $A^2 = 38$. $A^3 = 82$. $A^4 = 130$.

If, instead of placing tellurium in this group, we insert in the group one of its constituents on the assumption that ordinary tellurium is a *mixture*, *alloy*, or *compound* of the true tellurium with Argon No. 4, or tetrargon, adopting Mendeléeff's nomenclature, it would consist of equal parts—atoms—of true tellurium and tetrargon, for $\frac{125{\cdot}4 + 130}{2} = 127{\cdot}7$.

It is well known that "didymium" has been shown to be a mixture of two elements of nearly identical atomic weights which must be placed very near to each other in the system. Their discovery was rendered possible by the study of the absorption spectrum of didymium first observed by Gladstone. This last circumstance, however, does not hold good in a similar case, that of lanthanum, and although I found long ago that this may be separated by fractionation into portions, the "atomic weight" of which varies between 138·2 and 140, hitherto the absence of an absorption spectrum has proved to be a serious drawback in the study of this question.* Regarding tellurium from a similar point of view, we are struck by the fact that equal atomic proportions of true tellurium and tetrargon will have exactly the atomic weight 127·7, so that our ordinary tellurium might be a compound of the formula $Te_1A^4_1$.

This view was developed by me at a meeting of the Bohemian Academy of Sciences, on March 1, 1895, and it is highly satisfactory to find that Lecoq de Boisbaudran (*Compt. rend.*, 1895, **120**, 361) has arrived at an identical conclusion from a perfectly different point of view; his new system being founded apparently on the law of harmony of spectral lines (he has calculated in this way the atomic weights of gallium and germanium). Accepting my nomenclature; this new group is $A^1 = 20{\cdot}0945$, $A^2 = 36{\cdot}40 \pm 0{\cdot}08$, $A^3 = 84{\cdot}01 \pm 020$, $A^4 = 132{\cdot}71 \pm 0{\cdot}15$, but he places it in a still greater proximity to the group: O S Se Te.

The above equation becomes $\frac{122{\cdot}7 + 132{\cdot}7}{2} = 127{\cdot}7$.

I do not believe that the affinity of A^4 for other elements will be quite as small as that of the lower members, and I expect that Lord Rayleigh and Dr. Ramsay, by the study of argon, will be able to show us the entirely new chemical direction in which the problem of separating tellurium into its constituents should be approached.

A full account of the results obtained will be given by me in due course to the Chemical Society.

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* The same is repeated in the case of cerium in the recently published note by the author (*Chem. News*, of June 14th, 1895, p. 283).

LX.—*Note on Liquation in Crystalline Standard Gold.*

By T. K. Rose, D.Sc., A.R.S.M., Assistant Assayer of the Royal Mint.

Alloys of gold with copper and silver have been examined by Professor W. C. Roberts-Austen (*Nineteenth Annual Report on the Mint*, 1888, 53—56) and M. Peligot (*Bull. de la Soc. d'Encouragement pour l'Industrie Nationale*, T. IV, 1889, 171), with the view of determining whether any segregation takes place in them on cooling from a molten state. As the result of these experiments, Roberts-Austen expressed the opinion that "gold alloyed with silver and copper, and properly mixed in the molten state, is practically homogeneous when solid." He suggested, however, that the development of crystallisation, and other remarkable changes produced in the structure of gold by the addition of minute quantities of lead, bismuth, &c. (*Phil. Trans.*, 1888, **179**, 339), may cause rearrangement in the constituents of the standard gold thus rendered impure. The experiments described below were made with the view of determining whether this is the case or not.

The standard gold employed was prepared by melting English sovereigns, and was found to consist of—

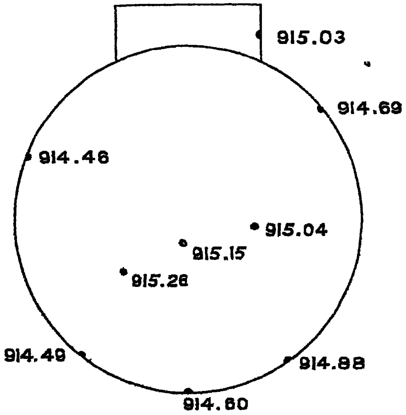
Gold	916·7
Silver	11·5
Copper (by difference)	71·8
	1000·0

It was rendered crystalline and brittle by adding to the molten metal small quantities of lead or bismuth, and in each case cast into a smoke-blackened, spherical iron mould, 3 in. in diameter, the weight of the gold ball being about 135 oz. The metal was poured as rapidly as possible, immediately after being thoroughly stirred, and the mould made hotter than in ordinary casting, the object being to fill the mould before solidification could begin. Under these conditions, sound castings were difficult to obtain, owing to the contraction of the mass, but the hollows sometimes formed at the "get," and, penetrating into the metal, did not appear to alter the results. The gold sphere was in every case very brittle, and was split into two halves without difficulty by a hammer and chisel. Samples were taken from various points and assayed for gold in triplicate, the results being subject to errors probably not exceeding ±0·02 per 1000 (see Trans., 1892, **61**, 700). On splitting open the spheres, there was found to be an outer layer, about ¼ in. thick, which had solidified quickly, differing markedly in structure from the interior of the mass. The outer layer was yellow, lustrous, and finely crystalline, whilst the interior had a redder colour and was less lustrous and more coarsely crystalline, faces of the octahedron being numerous. The appearance of the fracture was similar in all the experiments.

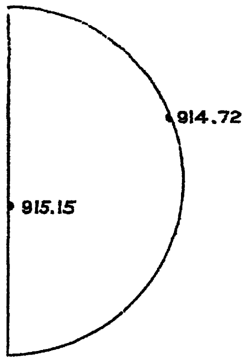
The chief results are appended.

I. Standard gold containing 0·2 per cent. of bismuth.

The figures on the diagrams give the fineness in gold of the metal at the indicated points. The diagrams represent sections through the centres of the spheres. B is a section at right angles to A.



A



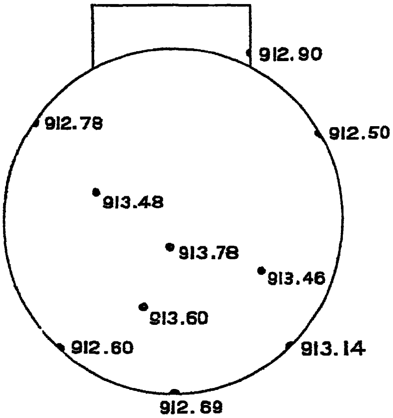
B

Means of assay results:—

Centre of sphere...	915·15
Interior of sphere (intermediate)........	915·15
Exterior of sphere	914·64
Difference	0·51

Maximum difference between inside and outside cuts, 0·8 per 1000.

II. Standard gold containing 0·4 per cent. of bismuth.



Means of assay results:—

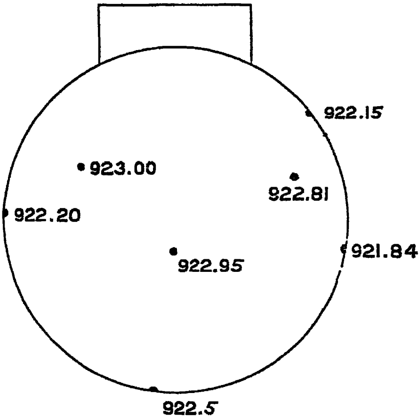
Centre of sphere	913·78
Intermediate	913·51
Exterior (15 assays)..........	912·74
Difference	1·04

Maximum difference between inside and outside of ball, 1·28 per 1000.

The structure was more coarsely crystalline than in No. 1.

The curve showing the rate of cooling of this ball was subsequently prepared by means of Roberts-Austen's recording pyrometer, but there was no perceptible sign of a second freezing point near the melting point of bismuth. This second freezing point has, however, more recently been observed by Roberts-Austen himself, using a more sensitive galvanometer in connection with the pyrometer, in the case of standard gold containing 0·4 per cent. of bismuth. He announced the result in his Third Report to the Alloys Research Committee, appointed by the Institution of Mechanical Engineers (p. 7, read April 26, 1895).

III. An alloy containing rather more gold than that present in standard gold was rendered brittle by the addition of 0·2 per cent. of lead.

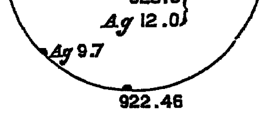


Means of assay results:—

Centre of sphere	922·95
Intermediate	922·90
Exterior (12 assays)	922·16

Maximum difference between the inside and the outside of the ball, 1·2 per 1000.

IV. The same metal melted and cast in a similar mould 2¼ in. in diameter.



Means of assay results.

Gold:	centre of sphere	923·00
	Intermediate	922·82
	Exterior	922·42
	Difference	0·58

Maximum difference between the inside and the outside of the ball, 0·6 per 1000.

Silver:	centre of sphere	12·0 per 1000
	Outside of sphere........	9·7 per 1000
	Difference......	2·3 per 1000

The exact position of the bismuth and lead in the various spheres was not ascertained. It is clear from the results, which were obtained over two years ago, that liquation takes place in standard gold if it has been rendered crystalline by either bismuth or lead, the centre of the mass becoming enriched in both gold and silver.

From this, it appeared probable that the lead and bismuth do not solidify with the main bulk of the standard gold, but remain melted until a much lower temperature is reached, the presence of the molten material enabling the part first solidified to assume a more definite crystalline form than would otherwise be possible. This has since been verified by Roberts-Austen, as mentioned above.

As the mass solidifies, beginning at the outside, the liquid bismuth and lead move towards the centre, carrying with them larger quantities of gold and silver than of copper, owing to the fact that the two former metals dissolve in bismuth or lead in greater proportion than the latter does. The liquation is thus readily accounted for.

It follows that the presence of such metals as lead and bismuth in unrefined gold bullion (which usually contains silver and copper) would render untrustworthy the system of valuation based on assays of pieces cut from the edges of ingots. The occasional discrepancies observed between assays of "dip samples" and "ouside cuts" are thus probably due to occurrence of liquation such as I have shown to take place.

LXI.—*Substitution-derivatives of Urea and Thiourea.*

By AUGUSTUS E. DIXON, M.D.

IN order to obtain the data required for an investigation in which the author has lately been engaged, it became necessary to verify the melting points of certain derivatives of urea, and of its sulphur analogue, and also to prepare a number of allied compounds, whose properties have not yet been recorded; the present communication is limited to a brief account of the principal experimental results thus incidentally obtained.

Determinations of melting point were made in narrow tubes, using a calibrated thermometer, and, in all cases, the observed temperatures are corrected for the exposed portion of the thread of mercury.

Thiourea Derivatives.

Trimethylthiourea, $CH_3\cdot N\colon C(SH)\cdot N(CH_3)_2$.—This was produced, with evolution of heat, on mixing methylthiocarbimide and dimethylamine in alcoholic solution. After twice recrystallising from benzene containing a little light petroleum, it formed colourless, thick, pointed prisms, melting at 87—88°. It is very freely soluble in water, alcohol, and chloroform, easily in hot benzene, more sparingly in cold; the benzene solution is precipitated by light petroleum. The alcoholic solution is blackened rapidly by ammoniacal, and slowly by neutral, silver nitrate, but is not desulphurised by boiling with alkaline solution of lead.

0·2402 gave 0·4655 $BaSO_4$. S = 26·64.
$C_4H_{10}N_2S$ requires S = 27·12 per cent.

Tribenzylthiourea, $C_6H_5\cdot CH_2\cdot N\colon C(SH)\cdot N(CH_2\cdot C_6H_5)_2$. — Prepared from benzylthiocarbimide and dibenzylamine, in alcoholic solution, and purified by recrystallisation from the same solvent; the crystals are very brilliant, silvery prisms, melting between 114·5° and 115·5°. It is insoluble in hot water, rather sparingly soluble in boiling alcohol, very sparingly in cold, moderately in warm ether, freely so in chloroform and benzene; the latter solution is precipitated by light petroleum. With silver and lead salts, it behaves like the corresponding trimethyl derivative.

Sulphur determination: 0·2392 gave 0·1671 $BaSO_4$. S = 9·60.
$C_{22}H_{22}N_2S$ requires S = 9·26 per cent.

When heated under ordinary pressure, it boils, gradually turning yellow, and decomposing with evolution of hydrogen sulphide and benzyl mercaptan.

ab*-*Phenylmetatolylthiocarbamide,* $C_6H_5\cdot NH\cdot CS\cdot NH\cdot C_6H_4\cdot CH_3$. — Two preparations were made, one from phenylthiocarbimide and metatoluidine, the other from metatolylthiocarbimide and aniline; in both cases the phenomena were alike. When mixed in alcoholic solution, no heat was evolved, nor was the odour of the thiocarbimide lost; the solution was therefore evaporated on the water bath until practically all the alcohol was expelled; the clear syrup thus obtained, slowly deposited tufts of crystals. After several recrystallisations from spirit, the substance formed hard, colourless, vitreous prisms, melting at 91—92°.

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* See note on the nomenclature of urea derivatives (p. 564).

Determination of sulphur (*m*ToNCS product).

0·2028 gave 0·2025 $BaSO_4$. S = 13·72.

$C_{11}H_{14}N_2S$ requires S = 13·23 per cent.

This compound is insoluble in water, almost indefinitely soluble in boiling alcohol, moderately in cold, easily so in ether, chloroform, carbon bisulphide, and benzene, very freely in acetone. It is moderately soluble in, and crystallises well from, hot light petroleum. The cold alcoholic solution is easily desulphurised by ammoniacal, or even by neutral, silver nitrate, and by alkaline lead solution, on warming.

ab-*Orthoparaditolylthiocarbamide*, $CS(NH{\cdot}C_6H_4{\cdot}CH_3)_2$.—This compound was obtained by Girard (*Ber.*, 1873, **6**, 445) from orthotolylthiocarbimide and paratoluidine, but no description of its properties is recorded, save that it occurs in silky needles, and is decomposed into its constituents by hot hydrochloric acid. Prepared from the above materials, and purified by repeated recrystallisation from alcohol, I obtained it in hard, vitreous prisms, melting at 172—173°, apparently undecomposed. It is insoluble in water, rather sparingly soluble in hot alcohol, and not much less so in cold; soluble in ether and chloroform, and easily in warm benzene. The solution is desulphurised by silver nitrate, or by boiling with alkaline lead tartrate.

ab-*Phenylmetaxylylthiocarbamide*, $C_6H_5{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_6H_3(CH_3)_2$.—Prepared by gently warming phenylthiocarbimide with metaxylidine [$NH_2 : Me_2$ = 1 : 2 : 3] in alcoholic solution; the product, a pinkish-white solid, after a couple of recrystallisations from spirit, separated in tufts of white needles, melting at 125·5—126°. The substance is almost insoluble in boiling water, moderately soluble in boiling alcohol or benzene, rather sparingly in cold, or in ether, freely in chloroform. It is readily desulphurised by silver or lead salts.

0·2578 gave 0·2352 $BaSO_4$. Or, S = 12·54.

$C_{15}H_{16}N_2S$ requires S = 12·51.

n-*Paratolyl-ν-dibenzylthiourea*,* $CH_3{\cdot}C_6H_4{\cdot}N{:}C(SH){\cdot}N(CH_2{\cdot}C_6H_5)_2$.—On adding paratolylthiocarbimide to dibenzylamine, both in alcoholic solution, heat was evolved, and the mixture set to a white paste. By draining and recrystallising the residue from much boiling alcohol, short, thick prisms and later, long, slender needles separated, both melting at the same temperature, namely, 145—146°. The compound is insoluble in water, sparingly soluble in alcohol or ether, easily in hot benzene (but with difficulty in cold), very freely so in chloroform. Ammoniacal silver nitrate blackens the solution only on warming; if boiled with alkaline lead tartrate, the solution turns clear yellow, but is not desulphurised.

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* See note on nomenclature, *post*.

0·2388 gave 0 1670 $BaSO_4$. S = 9·6.
$C_{22}H_{22}N_2S$ requires S = 9·26 per cent.

The following compounds, amongst others, were re-examined.

Secondary Butylthiourea.—From the thiocarbimide and alcoholic ammonia. Beautiful tufts of pearly prisms (from alcohol), m. p. 127·5—128·5°. Hofmann gives (*Ber.*, 1873, **6**, 513) 133°. Freely soluble in water, very freely in hot, and somewhat sparingly in cold, alcohol. Easily desulphurised by alkaline lead solution.

Isoamylthiourea.—From isoamylamine hydrochloride and potassium thiocyanate; after several recrystallisations from dilute spirit, it melted at 90—91° without undergoing decomposition (Hofmann, *Ber.*, 1870, **3**, 264, gives 93°). Almost insoluble in water, very freely soluble in alcohol; desulphurised by silver or lead solutions.

Parahydroxyphenylthiourea (from paraamidophenol hydrochloride and potassium thiocyanate, was found to melt at 220—221°. Kalckhoff (*Ber.*, 1883, **16**, 375) gives 214°.

ab-*Diparahydroxyphenylthiocarbamide* (from paramidophenol and carbon bisulphide), after four recrystallisations from alcohol, in which it is somewhat sparingly soluble, melted at 219—220°. Kalckhoff (*loc. cit.*, 1830) found it very freely soluble in alcohol, and its m. p. 222°.

Uns. (or *ν*) *Methylphenylthiourea* and ab-*Benzylphenylthiocarbamide* were found to melt at the temperatures already recorded.

Metatolylthiourea and *Dimetatolylthiocarbamide.*—Repeatedly recrystallised until the melting point was constant; the values found were 109·5—110·5° and 109—109·5° respectively. They differ slightly from those previously given (Trans., 1893, **63**, 328), namely, 110—111° and 111—111·5°, respectively.

ab-*Allylorthotolylthiocarbamide.*—When describing this compound (Trans., 1889, **55**, 622), I gave, through an oversight, the m. p. as 75—76°. Later on, Prager (*Ber.*, 1889, **22**, 2998), publishing an account of the compound as new, recorded the m. p. as 98°; on referring to my original specimen, I found the latter to be correct; the substance melts at 98—99°.

Urea Derivatives.

Isobutylurea, $(CH_3)_2CH{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}NH_2$.—Obtained by evaporating the mixed aqueous solutions of isobutylamine hydrochloride and potassium cyanate; the product was extracted with hot acetone and recrystallised from the same solvent. It formed slender, vitreous needles, having a spermaceti-like lustre and feel, becoming, when dry, strongly electrical on friction, and melting at 140·5—141·5°. The yield was about 55 per cent. of the theoretical.

0·186 gave 38 c c. moist nitrogen at 13° and 767 mm. N = 24·36.
$C_5H_{12}N_2O$ requires N = 24 19 per cent

The substance is very freely soluble in water, alcohol, and hot chloroform, moderately in boiling ether and benzene, sparingly in cold acetone, benzene, and chloroform.

Secondary Butylurea, $C_2H_5(CH_3)\cdot CH\cdot NH\cdot CO\cdot NH_2$.—Prepared from secondary butylamine hydrochloride and potassium isocyanate; the product was extracted with alcohol, the latter evaporated, and the residue taken up with warm acetone, from which, on cooling, the urea was deposited in very brilliant, large, flattened prisms. It dissolved freely in water, alcohol, and hot acetone, rather sparingly in cold, moderately in boiling, benzene, and melted at 169—170°.

0·2 gave 41·4 c.c. moist nitrogen at 15° and 764·5 mm. N = 24·35.
$C_5H_{12}N_2O$ requires N = 24·19 per cent.

ab-*Diisobutylurea*, $CO[NH\cdot CH_2\cdot CH(CH_3)_2]_2$.—This compound was obtained by desulphurising the corresponding thiocarbamide in hot alcoholic solution with silver nitrate.

It is strange that this method of preparing disubstituted ureas* seems not to have been already proposed, for, so far as my experiments have gone, it exhibits marked advantages over the ordinary processes. It is expeditious, the theoretical amount of desulphurising material can be taken with certainty, and the whole quantity added at once. Also, it is offered in solution, and therefore in a most efficient form; the yellow oxide of mercury which is sometimes used for the same purpose becomes superficially coated with sulphide, and its activity is thereby impaired. Moreover, in my experience, at least, the formation of sticky bye-products (often a source of trouble in the mercury process) is much lessened. In one or two cases there was some difficulty in completely removing the sulphur, but this was easily overcome by adding enough alcoholic potash to just neutralise the free nitric acid; this occurred only with paraffinoid compounds, in dealing with benzenoid derivatives no difficulty of the kind was encountered.

To *ab*-diisobutylthiocarbamide, dissolved in hot spirit, a little more than the theoretical amount of silver nitrate was added, the latter in concentrated aqueous solution, with which, immediately before use, its own volume of alcohol was mixed. Silver sulphide was at once precipitated, and after a few minutes warming, the solution was found to be free from sulphur. The silver sulphide was filtered off by aid of the pump, and on adding water to the clear filtrate, the urea separated in white needles, which, after recrystallisation from very dilute spirit, melted at 135—136°. The compound is practically insoluble in cold water, very freely soluble in alcohol.

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* And probably trisubstituted also: see methylphenylbenzylurea, *post.*

0·1823 gave 25·5 c.c. moist nitrogen at 14° and 768 mm. N = 16·62.
$C_9H_{20}N_2O$ requires N = 16·32.

ab-*Di-secondary-butylurea*, $CO[NH{\cdot}CH(CH_3)C_2H_5]_2$. — Secondary butylurethane was prepared by dropping ethylic chlorocarbonate into secondary butylamine, both substances in ethereal solution and cooled by a freezing mixture:

$$Cl{\cdot}COOEt + 2C_4H_9{\cdot}NH_2 = C_4H_9{\cdot}NH{\cdot}COOEt + C_4H_9{\cdot}NH_2,HCl.$$

The butylamine hydrochloride was removed by filtration, the ether evaporated from the filtrate, and the residual urethane distilled under atmospheric pressure; it is a colourless liquid, boiling at 193—195° (uncorr.).

By heating under pressure in a sealed tube for three hours at 210—240° with rather more than the calculated quantity of secondary butylamine, it decomposed as follows: $C_4H_9{\cdot}NH{\cdot}COOEt + C_4H_9{\cdot}NH_2 = CO(NH{\cdot}C_4H_9)_2 + EtOH$. After washing with acidulated water, the crystalline product was twice recrystallised from dilute spirit, and thus obtained in brilliant, pearly, flattened needles, melting at 137—138°.

0·2275 gave 32 c.c. moist nitrogen at 16° and 757 mm. N = 16·33.
$C_9H_{20}N_2O$ requires N = 16 32 per cent.

When boiled with water, it melts, dissolving to a moderate extent, and crystallising out again almost completely, on cooling; it is soluble also in benzene and in light petroleum.

ab-*Methylphenylurea*, $CH_3{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}C_6H_5$. Obtained by mixing phenylic isocyanate in ether, with methylamine in dilute alcohol. From hot alcohol, in which it is freely soluble (though sparingly so in the cold), it separates in broad, white, flattened prisms, moderately soluble in hot water, and hot benzene, and melting, without decomposition, between 150·5° and 151·5°.

0·1998 gave 32·4 c.c. moist nitrogen at 90° and 767 mm. N = 18·81.
$C_8H_{10}N_2O$ requires N = 18·71 per cent.

ab-*Secondary-butylphenylurea*, — $C_2H_5{\cdot}CH(CH_3){\cdot}NH{\cdot}CO{\cdot}NH{\cdot}C_6H_5$. By heating phenylurethane with excess of secondary butylamine in a sealed tube for several hours, at about 230°, a brown oil was formed, from which the above compound slowly separated. Sticky byeproducts occurred in considerable quantity, the removal of which entailed loss of nearly all the urea. The latter appears to be produced from secondary butylurethane and aniline, under like conditions, but the yield was even worse than by the converse method and the substance could not be obtained in a pure condition.

It was, however, easily prepared in quantity, by desulphurising *ab*-secondary-butylphenylthiocarbamide, in alcohol, with silver nitrate. The urea separated from hot alcohol in large, brilliant prisms, which, when purified by further recrystallisation, melted at 155·5—156·5°, undecomposed. It is insoluble in hot water, easily soluble in boiling alcohol, much less so in the cold.

0·1986 gave 25·1 c.c. moist nitrogen at 19° and 771 mm. N = 14·74.
$C_{11}H_{16}N_2O$ requires N = 14·62 per cent.

ab-*Phenylmetatolylurea*, $C_6H_5{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}CH_3$. — Prepared from silver nitrate and the corresponding thiocarbamide; by treatment with animal charcoal, and recrystallisation from boiling spirit, it was obtained in fine white needles, insoluble in water, easily soluble in hot alcohol, and melting at 173—174°.

0·2019 gave 21·6 c.c. moist nitrogen at 17° and 766 mm. N = 12·51.
$C_{14}H_{14}N_2O$ requires N = 12·42 per cent.

ab-*Phenylparatolylurea*, $C_6H_5{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}CH_3$.—From phenylic isocyanate in ether, and paratoluidine dissolved in anhydrous alcohol. It is insoluble in hot water, somewhat sparingly soluble in hot alcohol, and crystallises from the latter solvent in long, slender, flexible, white, needles, melting at 212—213°.

0·2057 gave 22 8 c.c. moist nitrogen at 22° and 767 mm. N = 12·59.
Theory, N = 12·42 per cent.

ab-*Orthoparaditolylurea*, $CO(NH{\cdot}C_6H_4{\cdot}CH_3)_2$.—The corresponding thiocarbamide was desulphurised with silver nitrate; after several recrystallisations from spirit, the urea formed very slender, flexible, white, needles, melting at 263—264°; it is insoluble in water, and only sparingly soluble in hot alcohol.

0·1998 gave 19 8 c.c. moist nitrogen at 18° and 775 mm. N = 11·67.
$C_{15}H_{16}N_2O$ requires N = 11·69 per cent.

ab-*Ethylbenzylurea*, $C_2H_5{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}C_6H_5$. — Silver nitrate was added to alcoholic ethylbenzylthiocarbamide; the filtrate (from Ag_2S) was mixed with water to incipient precipitation, and gave, on cooling, a copious crystallisation of pearly, flattened needles. By recrystallising from very dilute spirit, long, silky prisms were obtained; when dry they became highly electrical on friction, and melted between 104 and 105°.

0·2 gave 27·6 c.c. of moist nitrogen at 17° and 754·5 mm. N = 15·88.
$C_{10}H_{14}N_2O$ requires N = 15·76 per cent.

ab-*Benzylorthotolylurea*, $C_6H_5{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}CH_3$. — Obtained from silver nitrate and the corresponding thiocarbamide; the filtrate from Ag_2S, on cooling, deposited the substance almost pure. After recrystallisation from spirit, it occurred in small, vitreous prisms, insoluble in cold water, moderately soluble in hot alcohol, and melting at 188—188·5°.

0·201 gave 20·2 c.c. of moist nitrogen at 19° and 773 mm. N = 11·75.
$C_{15}H_{16}N_2O$ requires N = 11·69 per cent.

ab-*Benzylmetatolylurea*, $C_6H_5{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}CH_3$.—Prepared from benzylmetatolylthiocarbamide and silver nitrate; the compound deposited from the filtrate was practically pure. By recrystallisation from alcohol (whereby its melting point was raised by half a degree), it was obtained in slender, flexible, silvery needles, melting between 158·5° and 159°.

0·1996 gave 20·4 c.c. moist nitrogen at 16° and 764·5° mm. N = 11·98.
$C_{15}H_{16}N_2O$ requires N = 11·69 per cent.

The urea is insoluble in water, easily soluble in hot alcohol, moderately in cold, sparingly in cold ether or benzene; the last-mentioned solution is precipitated by adding light petroleum.

a-*Methyl*-b-*phenylbenzylurea*, $CH_3{\cdot}NH{\cdot}CO{\cdot}N(C_6H_5){\cdot}CH_2{\cdot}C_6H_5$.—In order to learn whether the silver process is applicable also to the preparation of trisubstituted ureas, the following experiment was made.

n-Methyl-*ν*-phenylbenzylthiourea (from methylic thiocyanate and benzylaniline) in boiling alcoholic solution was treated with silver nitrate; the filtered solution thrown into water, the resultant precipitate drained off and recrystallised from a mixture of benzene with light petroleum; the yield of pure substance, thus obtained, amounted to about 60 per cent. of the theoretical.

0·201 gave 20·4 c.c. moist nitrogen at 18° and 762 mm. N = 11·75.
$C_{15}H_{16}N_2O$ requires N = 11·69 per cent.

The urea forms pearly white crystals, becoming somewhat electrical on friction with a spatula, and melting between 107·5° and 108·5°. It is insoluble in water, very freely soluble in alcohol, ether, and chloroform; the benzene solution is precipitated by light petroleum.

The following, amongst other compounds of the same class, were prepared and examined, with the results stated below.

aa-*Dimethylurea.*—Melted at the temperature given by Franchimont (*Rec. Trav. Chim.*, 2, 129), namely, 180°. It is freely soluble in water.

Propylurea.—Crystallises from acetone in very thin, broad, ice-like plates; m. p., 107·5—108·5°. Chancel's figure (*Bull. Soc. Chim.*, 1893, [3], 9, 102) is 107°.

ab-*Dipropylurea*, from the corresponding thiocarbamide and silver nitrate melted, after three recrystallisations from weak spirit, at 106—107°. Hecht (*Ber.*, 1890, **23**, 285) found the m. p. 105°.

Isoamylurea, from isoamylamine hydrochloride and potassium isocyanate, melted at 92—93·5°. Custer, who prepared it from isoamyl isocyanate and ammonia (*Ber.*, 1879, **12**, 1333), found 89—91°.

Diisoamylurea.—As obtained by Custer (*loc. cit.*) from isoamyl isocyanate and isoamylamine, it formed whitish needles, melting at 37—39°. I first prepared it by heating isoamylurethane with isoamylamine, under pressure, at 230—240°, thereby obtaining pearly flattened prisms, half melting at about 48°, resolidifying one or two degrees higher, and remelting at 63—64°. The yield was very poor, about 0 5 gram from 15 grams of materials. It was more satisfactorily obtained, however, from the corresponding thiocarbamide and silver nitrate, the product, as before, really melting at 48°, solidifying at 51°, and melting again at 65—66°. It is excessively soluble in all the solvents tried, with the exception of water; and whether the behaviour on heating is peculiar to the substance, or due to some impurity, is still uncertain.

ab-*Ethylphenylurea*, from phenylic isocyanate and ethylamine; the melting point found was 100° sharp. Wurtz gives (*Compt. rend.*, **32**, 417) for the product from ethylic isocyanate and aniline, the melting point, 99°.

ab-*Allylphenylurea.*—Prepared (1), from phenylic isocyanate and allylamine, and (2), from allylphenylthiocarbamide and silver nitrate. Both products, when pure, melted at the same temperature, namely, 114·5—115 5°, and the former gave, on analysis, 15·91 per cent. of nitrogen, against 15·94 required by theory. The melting point given by Maly (*Zeit. f. Chem.*, 1869, 263) is 96—97°.

Note on the Nomenclature of Oxy- and Thio-urea Derivatives.

Some convention appears desirable, whereby the position, within the molecule, of the various substituting groups may be conveniently expressed in naming these compounds. For derivatives of carbamide and thiocarbamide, the method adopted by Beilstein in his "*Handbuch*," is quite satisfactory; the points of attachment at the two nitrogen-atoms, *e.g.*, thiocarbamide, being designated *a* and *b* respectively, thus—$S{:}C{<}\begin{smallmatrix}N<a\\N<b\end{smallmatrix}$; these letters, prefixed to the names of the radicles there attached, serve to define the positions of the latter. But amongst "labile" or thiourea* derivatives, the nomenclature is

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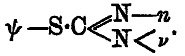
* It is proposed by Emerson Reynolds (Trans, 1889, **59**, 395), to distinguish between the true thiocarbamides and the $NH{:}C(SH){\cdot}NH_2$ forms, by calling the latter *thio-ureas*.

very confused, and I venture, therefore, by way of rendering it more precise, to suggest the following addition to the terminology. The NH and NH_2 attachments may be distinguished as *n* and *ν*, respectively; the compound, as proposed by Reynolds, being termed a thiourea; whilst if the sulphur attachment is occupied by a radicle, the compound may be designated a pseudothiourea, the radicle so linked, being placed first in the name, next the ψ symbol, and finally the rest of the atomic complex. The following diagram illustrates the scheme.



$$\psi-S\cdot C\begin{matrix}\nearrow N-n\\ \searrow N<\nu\end{matrix}.$$

Thus, for example, the systematic names of $EtN\colon C(SH)\cdot NMe_2$, $NH\colon C(SMe)\cdot NH_2$, and $EtN\colon C(SMe)\cdot NHEt$ would be, respectively, *n*-ethyl-*ν*-dimethylthiourea, methyl-ψ-thiourea, and methyl-ψ-*nν*-diethylthiourea. This nomenclature is obviously capable of extension to other more complex derivatives, as, for instance, the thiohydantoins.

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LXII.—*Derivatives of Succinyl and Phthalyl Dithiocarbimides.*

By Augustus E. Dixon, M.D., and R. E. Doran.

Numerous "mustard-oils" are known of the general type $R'NCS$ (where R' is a monad hydrocarbon residue), and a few of the form $R''(NCS)_2$, R'' being a dyad residue of the same kind. Some three or four monacidyl thiocarbimides have also been obtained, notably $CH_3\cdot CO\cdot NCS$ and $C_6H_5\cdot CO\cdot NCS$,* but the existence of dithiocarbimides of the acid class appears not to have been hitherto recorded.

We have therefore commenced an investigation in the latter direction, and beg now to lay before the Society an account of the principal results hitherto obtained.

Succinyldithiocarbimide.

Succinyl chloride and well-dried lead thiocyanate, in the proportions required by the equation

$$C_2H_4(CO\cdot Cl)_2 + Pb(SCN)_2 = PbCl_2 + C_2H_4(CO\cdot NCS)_2,$$

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* Obtained by Miquel (*Ann. Chim. Phys.*, 1877, [5], 11, 295; 300), from lead thiocyanate and the corresponding acid chlorides.

were mixed with anhydrous benzene, and heated on the water bath, shaking constantly. Before the boiling point was reached, action commenced with evolution of heat, and the solution became reddish-brown; the process was completed by adding a few more grams of lead thiocyanate, and heating for half an hour, using a reflux condenser. A brownish residue, consisting principally of lead chloride, was filtered off by means of the pump, and the filtrate, which was of a clear reddish-brown, was found to be free from chlorine, and possessed little odour save that of benzene; it gave, with alcohol and ammoniacal silver nitrate in the cold, a precipitate of silver sulphide, and was easily desulphurised by warming with alkaline lead tartrate, reactions indicating the presence of a thiocarbimide or one of its immediate derivatives.

By carefully evaporating most of the benzene at a gentle heat, a blackish oil was obtained, of pungent, tear-exciting odour, resembling that of acetylthiocarbimide, but it did not seem pure enough for analysis. Like the latter compound, it soon decomposes—even in the benzene solution—becoming dark coloured, and depositing a deep brown, pasty solid in small quantity.

An attempt was made to purify the substance by distillation in a vacuum, but it darkened considerably, and on raising the temperature slightly after the benzene had all come over, the mixture suddenly turned black, effervesced violently, and a sharp detonation occurred, shattering the distillation-flask. A strong odour of mushrooms was noticed.

Isolation by distilling in a steam current was out of the question, as the thiocarbimide proved to be decomposable by water; and after some further endeavours to precipitate it by means of light petroleum, which led to no definite result, an investigation of its derivatives was proceeded with.

In the experiments described below, the following method was generally adopted. A preliminary trial having shown that the yield amounted to over 90 per cent. of the theoretical, the product was further diluted with anhydrous benzene, so that every 5 c.c. should contain about 1 gram of succinyldithiocarbimide, and the freshly prepared solution was employed.

Succinyldithiocarbimide and Aniline. Succinyl-ab-*diphenyldithiourea*, $C_2H_4(CO{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_6H_5)_2$.

Nine grams (1 mol.) of the dithiocarbimide, in benzene, were carefully added to a cooled benzene solution containing 8·3 grams (2 mol.) of pure aniline. Interaction rapidly occurred, with evolution of heat, and in a very short time the contents of the vessel set to a paste. On draining off the entangled benzene by means of the filter pump, and washing the residue with fresh benzene, a finely-divided, brownish, amorphous solid was obtained, amounting, when dry, to 15·5 grams, or about 90 per cent. of the weight of the materials employed.

The powder was digested with a little hot acetone, which removed most of the colouring matter, and the residue dissolved in (much) boiling acetone; on cooling, beautiful, silky needles were deposited, almost colourless, and melting at 207—208°. By adding water to the mother liquor, and recrystallising the precipitate from boiling glacial acetic acid, the compound was obtained in felted masses of pure, white, hair-like needles, melting, with effervescence, to a reddish-brown liquid, at 210—210·5° (corr.). A complete analysis was made, with the following results.

0·2993 gave 0·6086 CO_2 and 0·1331 H_2O. C = 55·45 and H = 4·95.
0·1988 „ 24·8 c.c. moist nitrogen at 17° and 768 mm. N = 14·63.
0·2869 „ 0·3446 $BaSO_4$. S = 16·5.

These figures are in accordance with the formula

$$C_2H_4(CO{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_6H_5)_2.$$

	Theory. $C_{18}H_{18}N_4S_2O_2$.		Experiment.
C	55·90		55·45
H	4·67		4·95
N	14·54		14·63
S	16·59		16·51
O	8·30	(By diff.)	8·46

Succinyldiphenyldithiourea is very sparingly soluble in boiling alcohol, ether, or benzene, with difficulty in chloroform and ethylic acetate, more easily in boiling acetone or glacial acetic acid. It is insoluble in water and in boiling, concentrated hydrochloric acid, but dissolves freely in sulphuric acid or dilute caustic potash; the former solution is precipitated on adding water. If the latter be mixed with a few drops of lead solution, and heat applied, the tube becomes plated with a very brilliant galena speculum; the sulphur, also, is instantly withdrawn on adding silver nitrate to the warm alcoholic solution. Ferric chloride produces no colour change.

Action of Caustic Alkali.—A quantity of the pure dithiourea substance was dissolved, with gentle warming, in pure, dilute, caustic soda; on cooling, white prisms separated, which, after thorough washing with cold water, melted at 152—153° (uncorr.). Hydrochloric acid, when added, in very slight excess, to the clear filtrate from the crystals, threw down a copious precipitate of fine needles; these, when recrystallised from boiling water, occurred in well formed, pure white prisms, melting at nearly the same temperature as the former crop, namely, 154° (corr.). Both products were easily soluble in hot water, very sparingly in cold, freely in alcohol; the cold solution was blackened at once by ammoniacal silver nitrate, and yielded a fine mirror when heated with alkaline lead tartrate. These reactions, together with the appearance, intensely bitter taste, and melting point of the substance, characterise it as phenylthiourea (m. p. 154°).

When exactly neutralised, the hydrochloric acid filtrate gave, with ferric chloride, a reddish-brown precipitate, and with barium chloride, ammonia, and alcohol, a white, thereby showing the presence of a succinate. Caustic alkali therefore decomposes the phenylic derivative as follows.

$$C_2H_4(CO{\cdot}NH{\cdot}CS{\cdot}NHPh)_2 + 2KOH = C_2H_4(COOK)_2 + 2CSN_2H_3Ph.$$

Action of Alcoholic Ammonia.—Under the influence of this reagent, at a moderate temperature, a symmetrical disubstituted thiourea is converted, with loss of one of its radicles as amine, into a monosubstitution compound. Thus, from thiocarbanilide, Gebhardt obtained (*Ber.*, 1884, **17**, 3045) phenylthiourea and aniline; and from the dinaphthyl compound, similarly, naphthylthiourea and naphthylamine. Succinyldiphenyldithiourea, however, containing two different groups attached to the thiocarbonyl nuclei, might decompose in either (or possibly both) of the following ways.

$$(1.)\ C_2H_4(CO{\cdot}NH{\cdot}CS{\cdot}NHPh)_2 + 2NH_3 = C_2H_4(CO{\cdot}NH{\cdot}CS{\cdot}NH_2)_2 + 2PhNH_2$$

$$(2.)\ C_2H_4(CO{\cdot}NH{\cdot}CS{\cdot}NHPh)_2 + 2NH_3 = C_2H_4(CO{\cdot}NH_2)_2 + 2CSN_2H_3Ph.$$

that is, into succinyldithiourea and aniline, or into succinamide and phenylthiourea. An experiment was made as follows.

Another portion of the pure succinyldiphenyl compound was mixed with excess of alcoholic ammonia, and the turbid liquid heated for an hour at 120—130°; there was no pressure on opening the tube, and the contents had become almost perfectly clear. After standing for a short time, needles were deposited; these melted at 153°, and, after recrystallisation, at 154° (corr.), consisted, as shown by their properties, of phenylthiourea. A faint trace of thiocyanate was also found, due to partial attack of the phenylthiourea by the ammonia (Claus, *Ber.*, 1876, **9**, 694), and a barely detectable trace of aniline was present, due only to the decomposition in question, $CSN_2H_3Ph + NH_3 = NH_4{\cdot}SCN + NH_2Ph$. The action therefore appears to run according to equation (2) above. but the succinamide, unfortunately, was not isolated.

Succinyl-ab-*diorthotolyldithiourea*, $C_2H_4(CO{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_6H_4{\cdot}CH_3)_2$.

This compound was prepared in like manner to the preceding: 9 grams of succinyldithiocarbimide and 9·6 grams of orthotoluidine yielded 18 grams of dry product, or over 96 per cent. of the theoretical. The brownish, amorphous solid was dissolved in the least possible quantity (about a litre) of boiling glacial acetic acid, from which, on cooling, it separated in beautiful, sea-green prisms. By another recrystallisation from the same solvent, it was obtained in colourless, glassy needles, which melted, with copious effervescence, at the same temperature as the sea-green product, namely, 217—218° (corr.).

The formula was checked by a sulphur determination.

0·2074 gave 0·2290 $BaSO_4$. S = 15·18.

$C_{20}H_{22}N_4S_2O_2$ requires S = 15·47 per cent.

Silver sulphide is precipitated at once on adding silver nitrate to the warm alcoholic solution, and a brilliant mirror is formed by treatment with alkaline solution of lead. In its solubility relations, it closely resembles the corresponding phenyl derivative.

Succinyl-ab-*di-α-naphthyldithiourea*, $C_2H_4(CO{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_{10}H_7)_2$.

The constituents in benzene solution at once united, with evolution of heat, forming a cream-coloured solid, which darkened superficially on exposure to air. It is practically insoluble in water, alcohol, chloroform, acetone, ethylic acetate, acetic acid, carbon bisulphide, benzene, toluene, cumene, and light petroleum; soluble in concentrated sulphuric acid; the last solution, when diluted with water, gave a jelly-like precipitate, which could not be filtered. The substance dissolved also in hot nitrobenzene, but did not separate on cooling. It was shaken up repeatedly with alcohol, filtered with the aid of the pump, well washed with more alcohol, and dried; as thus obtained, it was a pure white, fine powder, not affected by exposure to air, and melting to a black liquid at 224—225° (corr.). A determination of sulphur was made.

0·2 gave 0·1914 $BaSO_4$ S = 13·15.

$C_{26}H_{22}N_4S_2O_2$ requires S = 13·18 per cent.

Ferric chloride gives no coloration. When mixed with alcohol and treated with ammoniacal silver nitrate, little change occurs, probably on account of the insolubility of the compound, but, on heating, the mixture blackens at once. It is also easily desulphurised by warming with alkaline solution of lead.

Symmetrical Succinyl-ab-*dimethyldiphenyldithiourea*, $C_2H_4[CO{\cdot}N{:}C(SH){\cdot}N(CH_3)C_6H_5]_2$.

This substance was obtained from the dithiocarbimide and methylaniline as a yellowish solid, which, after washing with benzene, became white. From its solution in boiling spirit, it was deposited in hard, colourless, seemingly rhombic, prisms melting at a much lower temperature than the isomeric tolyl derivative, namely, 138—139° (corr.).

0·20 gave 0·2253 $BaSO_4$. S = 15·48.

$C_{20}H_{22}N_4S_2O_2$ requires S = 15·47 per cent.

It is insoluble in water, ether, and carbon bisulphide, sparingly and slowly soluble in alcohol, chloroform, acetone, and benzene. Like the other compounds mentioned above, it dissolves in sulphuric acid (the solution is precipitated by the addition of water), and in cold. dilute alkali. The latter solution is precipitated by hydrochloric acid, and is desulphurised only to a very trifling extent by even prolonged boiling with alkaline lead tartrate. Warm nitric acid vigorously attacks the substance, yielding a greenish liquid, which, when mixed with excess of alkali, becomes turbid and intense crimson in colour.

Symmetrical Succinyl-ab-*diphenyldibenzyldithiourea*, $C_2H_4[CO{\cdot}N{:}C(SH){\cdot}N(C_6H_5){\cdot}CH_2{\cdot}C_6H_5]_2$.

Obtained, with evolution of heat, from succinyldithiocarbimide and benzylaniline; when recrystallised from boiling alcohol, it formed rosettes of slender, white needles, melting, without effervescence, at 137—138° (corr.), to an orange liquid.

It is insoluble in water, sparingly soluble in ether and carbon bisulphide, moderately in boiling alcohol or benzene, much less so in the cold, freely in acetone, chloroform, and sulphuric acid.

0·214 gave 0·1831 $BaSO_4$. S = 11·76.

$C_{32}H_{30}N_4S_2O_2$ requires S = 11·32 per cent.

This compound, like other tertiary thioureas (see Trans., 1893, 63, 318), is not desulphurised by boiling for a short time with alkaline lead tartrate.

Action of Caustic Alkali.—The substance dissolved readily in warm, dilute, caustic potash, but the solution soon began to become turbid, and a copious, finely divided precipitate then rapidly formed, the contents of the vessel setting so that it could be inverted without loss. The product was drained by means of the vacuum pump, and recrystallised from very dilute spirit, whereby it was obtained in brilliant, vitreous prisms, melting at 136—137°.

The recrystallised material is insoluble in water, practically insoluble in warm dilute potash, but easily soluble in hot alcohol. It is desulphurised at once by cold ammoniacal silver nitrate, or gradually by boiling with alkaline solution of lead. In respect of all the characters mentioned, it agrees with *aa*-phenylbenzylthiourea, melting at 136·5° (Werner, Proc., 1892, 96); its identity with this was further established by a sulphur determination.

0·20 gave 0·1929 $BaSO_4$. S = 13·26.

$CSN_2H_2(C_6H_5)(C_7H_7)$ requires S = 13·23 per cent.

Succinyl-ab-*diphenyldisemithiocarbazide*, $C_2H_4(CO{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}NH{\cdot}C_6H_5)_2$.

Theoretical proportions of dithiocarbimide and phenylhydrazine were mixed in benzene solution; the heavy oil, which at once separated, became almost solid after standing for several days. By warming with a little alcohol, most of the adherent red oil was extracted, the yellow, solid residue was then dissolved in boiling glacial acetic acid, and, to the clear hot solution, water was added to incipient precipitation. On cooling, the substance was deposited in cream-coloured crystals, which sintered at 210°, and melted, somewhat indistinctly, at about 220° (corr.).

0·2001 gave 0·2224 $BaSO_4$. S = 15·28.

$C_{18}H_{20}N_6S_2O_2$ requires S = 15·39 per cent.

This compound is insoluble in water, sparingly soluble in boiling alcohol, moderately easily in warm, dilute, caustic potash. The latter solution* is not affected by continued boiling with alkaline lead tartrate, neither is the hot alcoholic solution desulphurised by ammoniacal silver nitrate.

Diethylic Succinyl-di-β-thiocarbamate, $C_2H_4(CO{\cdot}NH{\cdot}CS{\cdot}OC_2H_5)_2$.

Four grams of the dithiocarbimide, in benzene solution, were mixed with excess of anhydrous ethylic alcohol. No perceptible rise of temperature occurred, but, after about 12 hours' standing, the deep red colour of the mixture began to change to greenish-brown, and granular masses of crystals, having a beautiful, delicate sea-green colour, were slowly deposited, the separation being complete after three days. By recrystallisation from boiling alcohol, the compound was obtained in tufts of thick, white prisms, melting at 166—167° (corr.), with effervescence and separation of a white, crystalline substance.

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* Hydrochloric acid gave a precipitate with the potash solution, but this, on analysis, proved to be unchanged semithiocarbazide.

A sulphur determination gave figures agreeing with the formula of the di-β-thiourethane.

0·2007 gave 0·317 $BaSO_4$. S = 21·71.

$C_{10}H_{16}N_2S_2O_4$ requires S = 21·94 per cent.

$$C_2H_4(CO{\cdot}NCS)_2 + 2C_2H_5{\cdot}OH = C_2H_4(CO{\cdot}NH{\cdot}CS{\cdot}OC_2H_5)_2.$$

Succinyldithiodiurethane is insoluble in water or carbon bisulphide, and nearly so in ether. It dissolves sparingly in chloroform and benzene, moderately in boiling alcohol, much less so in cold. The solution in weak spirit gives no coloration with ferric chloride; with ammoniacal silver nitrate, a white precipitate falls, which blackens on heating; the sulphur is also removed by boiling with alkaline lead tartrate. When heated alone, the substance decomposes with effervescence and evolution of hydrogen sulphide and ethyl mercaptan.

Between alcohol and succinyldithiocarbimide the interaction goes very smoothly; the mixture, as already mentioned, does not become sensibly warm, neither are sticky bye-products formed; the substance deposited, save for a faint greenish coloration, is pure, and the yield is fair. With acetylthiocarbimide and alcohol, on the other hand, as previously recorded by one of us (Trans., 1892, 61, 529), the action is almost explosively violent and the decomposition profound; instead of acetylthiourethane, the products were ethylic acetate, thiocyanic acid, pseudosulphocyanogen, and free (fused) sulphur.

Action of Water on Succinyldithiocarbimide.

Two grams of the thiocarbimide in benzene were added to excess of cold water, the mixture frequently shaken, and the benzene allowed to evaporate gradually at the ordinary temperature. A small quantity of brownish, amorphous powder was removed by filtration, and the clear filtrate examined; it was strongly acid to test-paper, and gave, with ferric chloride, an intense thiocyanic reaction; when just neutralised, it gave, with the same reagent, a dull brownish-red, amorphous precipitate, and, with barium chloride, ammonia, and alcohol, a white precipitate. The main decomposition may accordingly be represented as follows.

$$C_2H_4(CO{\cdot}NCS)_2 + 2H_2O = C_2H_4(COOH)_2 + 2HSCN;$$

it does not, however, occur quantitatively, for not only is the brown, amorphous powder formed (the quantity of this was too small for investigation), but, in addition, the aqueous solution contains a substance—the amount of which diminishes gradually on keeping—which is desulphurised by boiling with alkaline lead tartrate.

Action of Alcoholic Ammonia on Succinyldithiocarbimide.

To the cooled thiocarbimide, a considerable excess of alcoholic ammonia was added; the mixture became warm, and an olive-coloured solid was deposited, accompanied by a clear, brownish oil. By recrystallisation, first from alcohol and next from alcohol and animal charcoal, the former was obtained in white needles, free from sulphur, soluble in hot, but only sparingly in cold, water, insoluble in absolute alcohol, melting at 241—242°, and consisting of succinamide (m. p. of succinamide, 242—243°). Analysis showed the substance to contain 24·38 per cent. of nitrogen; $C_2H_4(CO{\cdot}NH_2)_2$ contains 24·25.

Owing to an accident, the oily product was lost; the reaction, however, probably runs in two stages as follows.

(1.) $C_2H_4(CO{\cdot}NCS)_2 + 2NH_3 = C_2H_4(CO{\cdot}CSN_2H_3)_2$.

(2.) $C_2H_4(CO{\cdot}CSN_2H_3)_2 + 2NH_3 = C_2H_4(CO{\cdot}NH_2)_2 + CSN_2H_4$,

that is, succinyldithiourea is first formed, and decomposes then with the excess of ammonia, as in the case of the phenylated analogue.

Further experiments were now made with the view of obtaining a benzenoïd analogue of succinyldithiocarbimide. A mixture of phthalyl chloride with dry lead thiocyanate in molecular proportions was gently warmed in presence of benzene; it soon began to turn reddish, and a vigorous action commenced, the solution boiling briskly of itself for some time; the process goes rapidly in this case, for, after further heating for a couple of minutes to the boiling point, the liquid was free from chlorine. A yellow, solid residue, consisting mainly of lead chloride, was removed by means of the filter-pump, and washed well with benzene; the filtrate, rich scarlet in colour, was further diluted, as in the case of the succinyl compound.

At the ordinary temperature, the benzene solution soon changed, even in a vacuum, and a little deep red, sticky semi-solid was deposited; on evaporating the benzene, dark reddish crystals separated, which, after washing with benzene, melted at 112—113° to a pasty, brômine-coloured liquid, but could not be obtained fit for analysis; they were probably the impure thiocarbimide, produced thus—

$$C_6H_4(CO{\cdot}Cl)_2 + Pb(SCN)_2 = C_6H_4(CO{\cdot}NCS)_2 + PbCl_2.$$

The benzene solution, when mixed with spirit, is easily desulphurised by silver and lead salts.

Action of Water.—The experiment was carried out as in the case of the succinyl analogue, the phenomena being similar to those already described. The solution became strongly acid, and thiocyanic acid was found to be present, together with phthalic acid (m. p. observed, 203 corr.); in addition, a brownish semi-solid was formed, insoluble in water, and the aqueous solution contained a trifling quantity of a substance desulphurisable by boiling with alkaline lead tartrate.

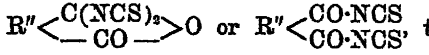
Action of Bases.—Numerous experiments were made, using various bases, but with unsatisfactory results, the products usually separating as viscid pastes, hardening partially on keeping. By pouring off the benzene, digesting the residues with cold alcohol, and recrystallising, some of the compounds were obtained approximately pure, but always in very limited quantity.

Thus, from *aniline*, a substance was obtained which separated from hot acetic acid in fine needles, moderately soluble in hot alcohol, desulphurised by silver, but not by lead salts, softening at 208°, and melting at 210—211° (corr.). The *orthotoluidine* product, after being well washed with spirit, formed a cream white powder, sintering at 175°, and melting at 177—178° (corr.). It dissolved, like the succinyl analogues, in warm, dilute potash, and, on the addition of hydrochloric acid to the solution, it gave white needles melting at 160—161° (m. p. of orthotolylthiourea, 160—161°; Trans., 1892, **61**, 525). *Benzylamine* gave rosettes of white needles, sparingly soluble in alcohol, softening at 161°, and melting at 163°. The *naphthylamine* and *benzylaniline* compounds were not obtained even approximately pure. With secondary *butylamine*, a clear, reddish oil was produced, insoluble in water, sparingly soluble in benzene, miscible with alcohol, and desulphurised by silver or lead solutions.

Sulphur found = $15{\cdot}82$; Cal. for $C_6H_4(CO{\cdot}NH{\cdot}CS{\cdot}NHBu)_2$, S = $16{\cdot}25$ per cent.

Methylaniline yielded a substance crystallising from alcohol in vitreous prisms, and melting at 188—189° (corr.). It is not desulphurised by alkaline lead solution, but gives up its sulphur to ammoniacal silver nitrate, on warming. It is vigorously attacked by hot, fuming nitric acid, with production of a substance crystallising in pale yellow needles, melting at 127°, and possessing all the properties of trinitrophenylmethylnitramide, $C_6H_2(NO_2)_3{\cdot}NMe(NO_2)$. These compounds are still under investigation.

In the absence of any means of deciding, on the data so far obtained, whether the formulæ of (*e.g.*) the thiocarbimides should be written



$R''<\substack{C(NCS)_2\\ \text{—}CO\text{—}}>O$ or $R''<\substack{CO{\cdot}NCS\\ CO{\cdot}NCS}$, the latter has been provisionally adopted. With respect, moreover, to some of the thiourea derivatives, there is the same uncertainty regarding the structure of the "thiocarbamidic" fraction of the molecule, which still attaches to compounds produced from mustard oil and secondary amine. Thus, for example, assuming the symmetrical constitution for succinyldithiocarbimide, the product of its union with benzylaniline may be represented either as (1) $C_2H_4(CO{\cdot}NH{\cdot}CS{\cdot}NPhBz)_2$, or (2) $C_2H_4[CO{\cdot}N{:}C(SH){\cdot}NPhBz]_2$. From experiments made by Billeter and Strohl (*Ber.*, 1888, **21**, 106), it seems probable that the normal* trisubstituted thioureas are of the form $XN{:}C(SH){\cdot}NYZ$; a similar formula (2) has accordingly been used to represent the corresponding dithioureas.

Judging from the results described in this communication, and from other similar experiments (Miquel, *loc. cit.*), it appears that the interaction between lead thiocyanate and an acid chloride is as definite and generic as that between the alkylogens and potassium thiocyanate.

But whilst, in the latter case, an alkylic thiocyanate alone is produced, in the former, on the other hand, the product is a thiocarbimide, practically free from thiocyanate, saving what little may be formed owing to the presence of traces of moisture. Whether the lead salt itself functions as a thiocarbimide, or whether the acid radicle is specially concerned in the rearrangement of the SCN-group, is still under investigation.

It is curious that the earliest discovered acid thiocarbimide, $CH_3{\cdot}CO{\cdot}NCS$ (Miquel, *loc. cit.*), notwithstanding its activity, and the fact that, when treated with amines, it afforded well-marked thiocarbamide derivatives, was expressly regarded as a thiocyanate. Possibly its ready decomposition in contact with water is accountable for this—$CH_3{\cdot}CO{\cdot}NCS + H_2O = CH_3{\cdot}COOH + HSCN$.

But the production of thiocyanic acid, does not necessarily involve the view that the parent compound is a thiocyanate; the formation of this acid is easily explained by supposing that hydrogen thiocarbimide, H·NCS, is first liberated, and thereupon undergoes isomeric rearrangement into the more stable form. It seems also quite possible that the substance produced by the interaction of these thiocarbimides with water, which at first strongly desulphurises alkaline lead solution, but gradually, on keeping, almost entirely loses this power, may be H·NCS, slowly reverting, in dilute solution, to H·SCN.

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* As distinguished from "pseudo"-thioureas, in which the sulphur is directly engaged with an alkyl group.

LXIII.—*Affinity of Weak Bases.*

By JAMES WALKER, D Sc, and EMILY ASTON, B.Sc.

THE subject of the comparative strengths of weak organic bases has been several times under investigation during the past five or six years. The results obtained, however, are by no means so harmonious as could be desired, so that it appeared to us of interest to apply a new experimental method to the problem, in the hope of arriving at results in conformity with those obtained by one or other of the previous observers. As a basis of the method, we adopted the principle, first applied by one of us (Walker, *Zeit. physikal. Chem*, 1889, **4**, 319) and since used by other investigators, of balancing the base against a constant quantity of water; in other words, of measuring the extent to which equivalent solutions of the hydrochlorides of the bases are resolved into free acid and free base by the action of the water in which they are dissolved. The weaker the base the greater is the amount of hydrolysis, and this amount may be measured by estimating the quantity of free acid in the solution, either by means of some physical property or by the acceleration of some chemical action. As an example of the first method we have the electrical conductity (Walker, *Zeit. physikal. Chem.*, 1889, **4**, 333; Bredig, *ibid.*, 1894, **13**, 317), and of the second, the catalysis of methylic acetate (Walker, *loc. cit.*, 321). Lellmann and his pupils employed an equilibrium method for determining the strength of bases, but as they used a colorimetric process with a hydrolysable salt as indicator, the equilibrium was in their case often very complicated and led to results not easy of interpretation (Lellmann and Gross, *Annalen*, **260**, 262, and **263**, 286; Lellmann and Görtz, *Annalen*, **274**, 121).

The method we describe in this paper is an acceleration method, the magnitude measured being the rate of inversion of cane sugar by comparable solutions. This rate is roughly proportional to the amount of free hydrochloric acid in the solution, so that by determining it we at once get a measure of the approximate amount of hydrolysis of the dissolved salt. The influence of dilution, temperature, the presence of foreign compounds, &c., on the rate of inversion has been thoroughly investigated by Ostwald (*J. pr. Chem*, [2], **29**, 385; **31**, 307), Spohr (*J. pr. Chem.*, [2], **32**, 31; **33**, 265; *Zeit. physikal. Chem*, **2**, 194), and Arrhenius (*Zeit. physikal. Chem.*, **4**, 226). The results obtained by them are sufficient to indicate that while it would be a matter of considerable difficulty to estimate by this means the exact extent of hydrolyis in a solution of aniline hydrochloride, for example, still it would be a comparatively simple matter to determine whether the aniline salt were hydrolysed more or less than the corresponding salt of an analogous base in equivalent solution.

After several preliminary trials, we fixed upon 60° C. as the temperature of experiment, for at that temperature the inversion by salts of the weakest bases proceeds sufficiently slowly, and by salts of the stronger bases sufficiently rapidly to allow of convenient manipulation within the course of an ordinary day's work. The bath used for heating the solutions was a cylindrical metal vessel filled with water and provided with a stirring apparatus and thermoregulator such as are employed in the Ostwald-Arrhenius conductivity apparatus. In this case, however, the bulb of the thermoregulator was vertical and above the stirrer, and not horizontal and below it as usual. A tightly fitting lid closed the bath, short tubes being fitted in it to allow of the insertion of the regulator, the thermometer, and the test-tubes containing the solutions. A small central hole gave passage to the shaft of the stirrer. The thermometer employed was divided into fifths of a degree, and the temperature as a rule did not vary more than a tenth of a degree from the mean temperature of experiment.

The test-tubes to contain the solutions were heated for several hours with strong hydrochloric acid, and afterwards treated with steam in order to minimise the action of the aqueous solutions on the glass (compare Ostwald's *Manual of Physico-chemical Measurements*, 249). The sugar solution used in the experiments was made by dissolving 200 grams of pure, crystallised cane sugar in 1 litre of water, filtering the solution, and then boiling it for three-quarters of an hour with a reflux condenser. After it had cooled, 2 c.c. of pure chloroform were added, and the flask fitted with a sterilised stopper and siphon. The solution prepared in this way kept perfectly clear for over three weeks.

The bases were purified before use either by distillation or by crystallisation. A quantity was accurately weighed off, and to it was added a volume of hydrochloric acid of known strength scarcely sufficient for its complete neutralisation. A slight excess of base is rendered necessary by the fact that the effect of any excess of acid is proportional to that excess and large in comparison with the total effect, while the effect of an excess of base is comparatively very small. Experiments at various dilutions were made, and finally the dilution 1/30-normal was selected as the most convenient. The solutions of the hydrochlorides were, therefore, made 1/15-normal, as each was afterwards mixed with its own volume of sugar-solution. The mixture was made in the test-tube placed in position in the thermostat, both solutions being previously heated to 60°.

All readings with the polarimeter were made at 20°, that temperature being kept constant by a stream of water from a large reservoir flowing through a glass jacket which enclosed the observing tube.

The time at which the mixture of the solutions took place was noted, and at appropriate intervals 10 c.c. of the solution were removed and added to 2·5 c.c. of a triple-normal solution of sodium acetate. The object of the sodium acetate (Trevor, *Zeit. physikal. Chem.*, 1892, **10**, 32) was to stop the inverting action of the free hydrochloric acid, its place being largely taken by acetic acid which inverts sugar solution very slowly. The rotation of the resulting solution was then observed. The initial reading was obtained by diluting the sugar solution with its own volume of water, instead of with a corresponding volume of the hydrochloride. For the final reading, the sugar solution was mixed with an equal volume of hydrochloric acid solution, and heated at 100° to accelerate the inversion. The solutions remained in the thermostat for periods varying from one hour with the weakest bases to 5½ hours with the strongest. A tendency of the solution to become brown was observed in the case of most of the aromatic bases, but this discoloration did not as a rule proceed so far as to interfere seriously with the polarimetric readings.

The formula according to which the inversion proceeds is

$$\frac{\log(a_0 - A) - \log(a_n - A)}{t_n} = C.$$

A is the final reading, a_0 the initial reading, and a_n the reading at the time t_n reckoned in minutes from the moment of mixing. C is the velocity constant, which is roughly proportional to the quantity of hydrochloric acid in the solution.

The following numbers were obtained for 1/30-normal hydrochloric acid without the addition of a base.

Hydrochloric Acid.

I.

t.	a.	$a - A$.	C.
0	10·62	14·02	—
32·2	2·62	6·02	0·0114
42·7	1·27	4·67	0·0112
52·2	0·20	3·60	0·0113
	A = −3·40	Mean	0·0113

II.

t.	*a*.	*a* − A.	C.
0	10·62	14·02	—
31·9	2·73	6·13	0·0113
42·3	1·25	4·65	0·0113
52·0	0·17	3·57	0·0114

A = −3·40 Mean 0·0113

When an equivalent of pyridine was added to the hydrochloric acid, the constant was diminished as follows.

Pyridine Hydrochloride.

t.	*a*.	*a* − A.	C.
0	10·63	13·95	—
138	9·68	13·00	0·000223
238	9·05	12·37	0·000219
332	8·47	11·79	0·000220

A = −3·32 Mean 0·000221

Here the value of the constant C is almost exactly one-fiftieth of the value for hydrochloric acid alone, that is, if we assume strict proportionality between the constant and the amount of acid affecting the inversion, 2 per cent. of the pyridine hydrochloride is decomposed by the water into pyridine and free hydrochloric acid, the remaining 98 per cent. being unaffected. This proportionality, however, is disturbed by various circumstances. Firstly, even in solutions of hydrochloric acid alone of different concentrations, the proportionality is not exact, varying somewhat not only with the degree of electrolytic dissociation but also independently of this. Again, the presence of a neutral salt of the acid has considerable influence on the rate of inversion of the sugar. This source of uncertainty of course assumes large proportions in the case of strong bases like pyridine, where the concentration of the undecomposed salt is about fifty times that of the free acid. An idea of the magnitude of this influence may be obtained from the following table taken from Arrhenius (*Zeit. physikal. Chem.*, 1889, 4, 239).

		C′.
0·01-*n* HBr	—	31·9
„	+ 0·025-*n* KBr	32·2
„	+ 0·1-*n* KBr	33·9
„	+ 0·4-*n* KBr	38·5

Here we have the inversion constant of centinormal hydrobromic acid increased 20 per cent. when the acid acts in presence of potassium bromide 40 times more concentrated than itself. This increase is, however, in the case of the hydrochlorides, to a certain extent balanced by the influence of increasing dilution of the acid above alluded to, which *diminishes* the value of the constant. Thus we may take it that the ratio of the constant of the hydrochloride to the constant of hydrochloric acid at the same dilution affords a fair approximation to the amount of hydrolysis in a 10 per cent. sugar solution. It does not follow that this amount is the same as the hydrolysis which would take place in pure aqueous solution, for, even though the presence of the sugar may exert no specific action, it, in any case, diminishes the amount of water present in a given volume.

The tables which follow contain the results obtained for the other organic bases investigated. Bases of closely corresponding strengths were heated in the thermostat together, so that the effect of any slight variations of temperature might, as far as possible, be eliminated.

Quinoline Hydrochloride.

t	*a.*	*a* − A.	C.
0	10·63	13·95	—
181	9·32	12·64	0·000237
261	8·77	12·09	0·000237
359	8·18	11·50	0·000233
	A = −3·32	Mean	0·000236

Paratoluidine Hydrochloride.

t.	*a.*	*a* − A.	C.
0	10·63	13·95	—
148	9·12	12·44	0·000335
238	8·32	11·64	0·000331
331	7·42	10·74	0·000346
	A = −3·32	Mean	0·000337

Orthotoluidine Hydrochloride.

t.	*a.*	*a* − A.	C.
0	10·63	13·95	—
120	8·52	11·84	0·000591
204	7·20	10·52	0·000601
292	5·83	9·15	0·000627
	A = −3·32	Mean	0·000606

Aniline Hydrochloride.

t.	*a.*	*a* – A.	C.
0	10·63	13·95	—
155	8·45	11·77	0·000475
238	7·38	10·70	0·000484
330	6·25	9·57	0·000495
A = –3·32		Mean	0·000485

Glycocine Hydrochloride.

t.	*a.*	*a* – A.	C.
0	10·63	13·95	—
18·9	8·77	12·09	0·00328
40·5	7·07	10·39	0·00316
58·5	5·53	8·85	0·00338
A = –3·32		Mean	0·00327

Acetamide Hydrochloride.

t.	*a.*	*a* – A.	C.
0	10·63	14·18	—
18·8	5·75	9·30	0·0097
38·0	2·22	5·77	0·0102
57·9	0·07	3·62	0·0102
A = –3·55		Mean	0·0101

Urea Hydrochloride.

t.	*a.*	*a* – A.	C.
0	10·63	14·18	—
19·5	5·40	8·95	0·0103
40·7	1·78	5·33	0·0104
59·0	– 0·13	3·42	0·0105
A = –3·55		Mean	0·0104

Thiourea Hydrochloride.

t.	*a.*	*a* – A.	C.
0	10·62	14·02	—
33·0	2·80	6·20	0·0107
43·6	1·18	4·58	0·0111
53·1	0·18	3·58	0·0111
A = –3·40		Mean	0·0110

Propionitrile Hydrochloride.

t.	*a.*	*a* − A.	C.
0	10·62	14·02	—
33·7	2·58	5·98	0·0110
44·5	1·13	4·53	0·0110
54·5	− 0·1	3·50	0·0111
	A = −3·40	Mean	0·0110

Asparagine Hydrochloride.

t.	*a.*	*a* − A.	C.
0	10·46	13·81	—
51·9	5·47	8·82	0·00375
61·7	4·70	8·05	0·00380
71·6	4·12	7·47	0·00372
	A = −3·35	Mean	0·00376

Methylaniline Hydrochloride.

t.	*a.*	*a* − A.	C.
0	10·46	13·81	—
163	9·30	12·65	0·000234
238	8·80	12·15	0·000234
311	8·27	11·62	0·000241
	A = −3·35	Mean	0·000236

No constants could be obtained with dimethylaniline, which darkened rapidly in the tube, and also separated as an oil when the

Base.	C.	Approximate hydrolysis per cent.
Dimethylaniline	?	?
Pyridine	0·000221	2
Monomethylaniline	0·000236	2·1
Quinoline	0·000236	2·1
Paratoluidine	0·000337	3
Aniline	0·000485	4·5
Orthotoluidine	0·000606	5·5
Glycocine	0·00327	29
Asparagine	0·00376	34
Acetamide	0·0101	90
Urea	0·0104	92
Thiourea	0·0110	97
Proprionitrile	0·0110	97
(HCl	0·0113)	

solution of hydrochloride was added to the solution of sodium acetate. The rotations, however, showed that that base was a strong one, the numbers being smaller than those for any other substance investigated.

When arranged in the order of the constants C, the bases appear as on p. 582, the strongest base being placed first in the list.

It will be observed that the aromatic bases are very much stronger than the other bases examined, the amount of hydrolysis not being more than about 5 per cent. In the case of thiourea and propionitrile, on the other hand, the hydrochloride scarcely exists as such in aqueous solution. Urea and acetamide form somewhat more stable hydrochlorides than these, and the amido-acids, glycocine, and asparagine, are comparatively strong bases. For the weaker bases, from glycocine downwards, we have numbers determined from the catalysis of methylic acetate (Walker, *loc. cit.*, p. 339). These give the bases in practically the same order of strength as found by the sugar inversion method. The only difference is that whilst the inversion method makes acetamide slightly stronger than urea, the catalytic method makes it slightly weaker. A repetition of the experiments by the last method did not remove the discrepancy, but it would seem that the effect of an excess of acetamide on the inversion, &c., is greater than is the case with other bases.

With regard to the aromatic compounds investigated, the experimental evidence as to their relative strengths cannot yet be said to be final. Lellmann and Görtz (*Annalen*, **274**, 140) give the following order of strength:

	K.
(1) Paratoluidine	103·0
(2) Dimethylaniline	101·9
(3) Pyridine	76·7
(4) Aniline	67·5
(5) Orthotoluidine	54·0
(6) Quinoline	49·7

whilst we find—

	Hydrolysis.
(1) Dimethylaniline	1·5
(2) Pyridine	2·1
(3) Quinoline	2·1
(4) Paratoluidine	3·0
(5) Aniline	4·5
(6) Orthotoluidine	5·5

The greatest divergence lies in the positions in the table of paratoluidine and quinoline respectively. We make quinoline a much stronger base than Lellmann and Görtz find, and paratoluidine a much weaker base. The catalysis of methylic acetate, under the conditions previously employed (*Zeit. physikal. Chem.*, 1889, **4**, 319), is inapplicable to the comparatively strong aromatic bases, and the electrical method adopted in the same paper also gives results open to question, as Bredig has shown (*loc. cit.*). The very complete research of Bredig on the velocities of the positive organic ions has enabled him, however, to avoid the doubtful assumptions formerly adopted, and he has determined a constant for three of the above-mentioned bases which is independent of the dilution and may be accepted as a measure of their affinity. The constant, namely, is the ratio of the degree of dissociation of the hydrated bases to that of water. He finds the following numbers.

Paratoluidine................	132000
Aniline......................	41000
Orthotoluidine...............	29000

Here the three bases are in the same order as that found by us, and also by Lellmann and Görtz. Bredig's numbers afford us the possibility of checking the rough hydrolysis values we have given above.

	I.	II.
Paratoluidine........	1·53	3·0
Aniline..............	2·63	4·5
Orthotoluidine.......	3·07	5·5

In Column I are the real values of the hydrolysis at 25° in $\frac{1}{32}$-normal solution, whilst Column II contains the rough values at 60° in $\frac{1}{30}$-normal solution. The latter, it will be seen, are almost double the former; part of the divergence is, no doubt, due to the difference of temperature, but the sources of error previously indicated are probably responsible for the greater portion.

To obtain an accurate affinity constant for a base, the amount of hydrolysis of its hydrochloride must be determined, not at one dilution only, but at a series of dilutions. We therefore made a number of experiments at other dilutions than $\frac{1}{30}$-normal, but, as the extent of hydrolysis was liable to considerable uncertainty, we did not pursue the matter further. The results we obtained, however, placed the bases in the same order as that given in our table.

It would appear, on the whole, that whilst the sugar inversion method is inferior to the exact electrical method for the stronger bases, and possibly to the catalytic method for the weaker bases, it is yet of service as giving comparative results throughout the whole range, from the strong aromatic bases down to substances such as propionitrile, which can scarcely be said to be basic at all, and may be used in cases where the other methods are inapplicable.

Experiments with Inorganic Salts.

Little or nothing has as yet been done towards determining the relative strengths of the weakly basic inorganic hydroxides, such as those of aluminium or zinc, although it is true that, in a few cases, special properties have been made use of to estimate the amount of hydrolysis of their salts in aqueous solution; for example, ferric chloride solutions have been studied by G. Wiedemann by the aid of their magnetic properties, and by Ewan from the colorimetric point of view.

We have endeavoured to apply the sugar inversion method to this problem, and the results of our experiments are recorded below. The experimental substances were zinc nitrate, lead nitrate, cadmium nitrate, and aluminium nitrate. Perfectly clear solutions of the pure salts in water were obtained, and their strength estimated by direct analysis. The experiments were conducted at 80°, in order that the inversion might proceed with sufficient rapidity in the case of the least hydrolysed salts.

The tables given beneath are arranged as previously.

Lead Nitrate, ½-normal.

t.	*a.*	*a* – A.	C.
0	10·50	13·53	—
151	5·25	8·28	0·00141
203	3·45	6·48	0·00158
259	1·65	4·68	0·00178
	A = –3·03	Mean	0·00159

Cadmium Nitrate, ½-normal.

t.	*a.*	*a* – A.	C.
0	10·50	13·53	—
172	9·92	12·95	0 000111
252	9·32	12·35	0·000157
321	8·68	11·71	0·000195
	A = –3·03	Mean	0·000154

Aluminium Nitrate, ½-normal.

t.	*a.*	*a* – A.	C.
0	10·50	13·53	—
45·7	3·15	6·18	0·0075
62·1	1·47	4·50	0·0077
76·8	0·33	3·36	0·0078
	A = –3·03	Mean	0·0077

It will be observed that C does not retain a constant value, but increases with the time. Another experiment gave the same result, the mean being C = 0·00158.

Zinc Nitrate, ½-normal.

t.	*a.*	*a* − A.	C.
0	10·50	13 53	—
188	9·55	12·58	0 000168
264	8·90	11·93	0·000207
335	8·17	11·20	0·000245

A = −3 03 Mean 0·000207

To obtain a standard of comparison, the inversion constant of 1/1000-normal nitric acid was determined at 80°.

Nitric Acid, 1/1000-*normal.*

t.	*a.*	*a* − A.	C.
0	10·50	13·53	—
159·4	3·00	6 03	0·00220
190·9	2·00	5 03	0·00225
233·5	0·88	3 91	0·00231

A = −3·03 Mean 0·00225

Another experiment gave a mean C = 0·00223. We thus see that a semi-normal solution (in equivalents) of lead nitrate inverts cane sugar at a somewhat slower rate than a milli-normal solution of nitric acid at the same temperature. The amount of free nitric acid in the nitrate solution is therefore only about 0 2 per cent. of the total nitric acid, that is, this is the approximate extent of hydrolysis. The other values, estimated in the same way, are given in the following table.

Nitrates.	C.	Hydrolysis per cent. in equiv. seminormal solution.
Cadmium........	0·000154	0·014
Zinc............	0·000207	0·019
Lead............	0 00159	0·15
Aluminium......	0·0077	0·7

Cadmium and zinc hydroxides are thus much more strongly basic than the hydroxides of lead and aluminium, which are more nearly allied in strength to the strongest organic bases studied in the previous part of the investigation.

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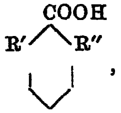
LXIV.—*Diortho-substituted Benzoic Acids. I. Substituted Benzoyl Chlorides.*

By J. J. Sudborough.

In previous papers published in the *Berichte* (1894, **27**, pp. 510, 1580, and 3146), it has been shown by V. Meyer and the author, that diortho-substituted benzoic acids of the type,



where R′ and R″ represent Br, Cl, NO_2, CH_3, or COOH, do not yield ethereal salts when their alcoholic solutions are saturated with dry hydrogen chloride. The diortho-substituted acids thus differ materially from their isomerides, all of which yield 90—100 per cent of ethereal salt when subjected to similar treatment.

Although the ethereal salts of these diortho-substituted acids cannot be prepared by saturating an alcoholic solution of the acid with hydrogen chloride, they are readily obtainable by either of the following methods:—(1) Treating the silver salt of the acid with an alkylic iodide. If the silver salt of the acid is heated on the water bath with an excess of methylic iodide, during half an hour, a theoretical yield of the methylic salt is obtained. The following have been prepared by this method.

Methylic 2 : 6-dibromobenzoate.
„ 2 : 4 : 6-tribromobenzoate.
„ 2 : 3 : 4 : 6-tetrabromobenzoate.
„ 2 : 4 : 6-trimethylbenzoate.
„ 2 : 4 : 6-trinitrobenzoate.

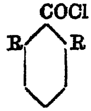
(2) By boiling the acid chlorides with the alcohol. In most cases substituted benzoates are produced by heating the corresponding acid chloride for a few minutes with excess of the alcohol; but in order to obtain the salts of the diortho-substituted acids it is necessary to boil the acid chloride for some time with the alcohol as the action seems to proceed more gradually.

The following have been obtained by this method.

Methylic orthobromobenzoate.
„ metabromobenzoate.
„ parabromobenzoate.
„ 2 : 4-dibromobenzoate.
„ 2 : 6-dibromobenzoate.

Methylic 3 : 5-dibromobenzoate.
,, 2 : 4 : 6-tribromobenzoate
,, 3 : 4 : 5-tribromobenzoate
,, 2 : 6-dinitrobenzoate.
,, 2 : 4 : 6-trinitrobenzoate.

In attempting to prepare the methylic salt of trichlorobenzoic acid, by the action of methylic alcohol on the acid chloride, it was found that if the two were merely heated together for a few minutes and then evaporated on the water bath the residue consisted of the unaltered chloride. On investigating the action of water on the acid chloride, it was found that on boiling the chloride with water for ten minutes, the merest trace of hydrogen chloride was liberated (Trans., 1894, **65**, 1030). V. Meyer about the same time observed that 2 : 4 : 6-trinitrobenzoyl chloride is also characterised by its stability in the presence of boiling water. These facts suggested the idea that acid chlorides of the type



are remarkably stable substances, and led to the research an account of which is contained in the following pages. As the basis of the work, the various bromobenzoyl chlorides were selected, as they were the most readily obtainable. The following were prepared and their stability studied.

Orthobromobenzoyl chloride.
Metabromobenzoyl ,,
Parabromobenzoyl ,,
2 : 4-dibromobenzoyl ,,
3 : 5-dibromobenzoyl ,,
2 : 6-dibromobenzoyl ,,
2 : 4 : 6-tribromobenzoyl ,,
3 : 4 : 5-tribromobenzoyl ,,
2 : 3 : 4 : 6-tetrabromobenzoyl ,,

The 2 : 6-dinitro- and 2 : 4 : 6-trinitro-benzoyl chlorides were also prepared, but on treatment with alkalis they were readily dissolved and deep red solutions were formed owing to secondary actions which took place (see V. Meyer, *Ber.*, 1894, **27**, 3156).

Decomposition with Water.—Preliminary experiments were made by boiling the acid chlorides for definite periods with a given quantity of water, and then estimating the amount of hydrogen chloride formed. The results of these experiments showed that the diortho-substituted chlorides are characterised by no great stability as compared with the other chlorides. Thus, of the three dibromochlorides, the 2 : 6-derivative was completely decomposed within 30 minutes, whilst the 3 : 5-derivative, under exactly the same conditions, required 40 minutes. The 2 : 4-chloride was entirely decomposed within 15 minutes. The two tribromochlorides were both very stable and were only slowly decomposed when boiled with water. The monobromobenzoyl chlorides show remarkable differences in their behaviour towards boiling water. Thus, whilst the ortho-derivative is entirely decomposed by boiling with water for two minutes, the meta-derivative requires 12 minutes for complete decomposition when boiled with the same quantity of water.

Decomposition with Sodium Hydroxide Solution.—A few preliminary experiments showed that the behaviour of the acid chlorides was quite different when boiled with dilute soda solution; thus, whilst most of them were immediately decomposed, those which contained bromine atoms in the 2 ortho-positions could only be converted into the sodium salts by boiling for some time with the alkali. In order to study the decomposition in each case, the following method was adopted :—An 8 per cent. solution of pure sodium hydroxide (prepared from metallic sodium and free from chlorine) was used. Half a gram of the chloride was heated, on a sand-bath, with 20 c.c. of this solution in a small flask connected with a reflux condenser. In many cases, the decomposition was complete within a few seconds after the solution began to boil; this was readily seen by the fact that all the chloride had disappeared and only a clear solution of the sodium salt of the acid remained. In those cases in which the action was not so vigorous, the course of the decomposition was followed by estimating the amount of hydrogen chloride formed at the expiration of a given time, the flask and its contents being rapidly cooled by plunging into a large beaker of cold water. The alkali solution was diluted with distilled water, the unaltered acid chloride filtered off, and the filtrate acidified with nitric acid. After being again filtered, if necessary, from any acid which might be precipitated, the hydrogen chloride in the clear solution was estimated by means of silver nitrate. The results thus obtained were checked by estimating the amount of unaltered acid chloride. To accomplish this the residue, which had been filtered off from the alkaline solution, was dissolved in pure ether (free from alcohol), dried over calcium chloride, the ether slowly evaporated, and the residue weighed. The two methods gave fairly concordant results.

Orthobromobenzoyl Chloride [COCl : Br = 1 : 2].

This is readily prepared by heating the orthobromo-acid with phosphorus pentachloride in molecular proportion. It is a colourless liquid, which distils at 245° (uncorr.), and has the characteristic acid chloride smell. On cooling in ice, it solidifies to a mass of colourless needles which melt at about 11°. It is only slowly acted on by cold, but rapidly by hot, water. The following numbers were obtained on boiling with water for two minutes.

	Weight of chloride.	Water.	Time.	AgCl.	Per cent. decomposed.
(1)	0·500 gr.	20 c c.	2 mins.	0·3270 gr.	100·03
(2)	0·500 „	20 „	2 „	0·3265 „	99·88

Decomposition with Sodium Hydroxide Solution (8 per cent.).—Half a gram of the acid chloride was boiled with 20 c.c. of the alkali solution; although the decomposition was rapid, a clear solution of the sodium salt of the orthobromo-acid was only obtained after the boiling had been continued for two minutes. The acid, which was precipitated on adding hydrochloric acid, melted at 147°. It would seem that this chloride is somewhat more stable than the corresponding meta- and para-compounds.

Methylic Salt, $C_6H_4Br\cdot COOCH_3$.—This was readily obtained by boiling the acid chloride for a few minutes with excess of methylic alcohol. It is a colourless oil, boiling at 250° (uncorr.). Rahlis (*Annalen*, 1879, **198**, 99) gives 246—247° as the boiling point.

Amide, $C_6H_4Br\cdot CONH_2$.—Strong aqueous ammonia reacts vigorously with the acid chloride, forming the amide which crystallises from boiling water in silky needles, melting at 155°. Schotten (*Ber.*, 1888, **21**, 2251) gives 155—156° as the melting point.

Metabromobenzoyl Chloride [COCl : Br = 1 : 3].

This chloride has already been prepared by Muller (*Zeit. für Chem.*, 1871, 301). It is a colourless oil, which has the characteristic pungent odour, boils at 243° (uncorr.) under atmospheric pressure, and does not solidify at 0°.

Decomposition with Water.—The following numbers were obtained on boiling with water.

	Chloride.	Water.	Time.	AgCl.	Per cent. decomposed.
(1)	0·5010 gr.	20 c.c.	4 mins.	0·1420 gr.	43·35
(2)	0·5000 „	20 „	8 „	0·3010 „	92·08
(3)	0·5000 „	20 „	12 „	0·3252 „	99·48

Decomposition with Sodium Hydroxide Solution.—Half a gram of the chloride, heated with 20 c.c. of the 8 per cent. soda solution, was completely decomposed within 10 seconds of boiling, with formation of the sodium salt of metabromobenzoic acid. The acid which was recovered from this alkaline solution melted at 155°.

Methylic Salt, $C_6H_4Br\cdot COOCH_3$.—This was prepared from the chloride and methylic alcohol. Recrystallised from methylic alcohol, it forms colourless plates which melt at 31°. Meyer and Ador give 31—32° as the melting point of the salt obtained by saturating with hydrogen chloride a solution of the acid in methylic alcohol.

Amide, $C_6H_4Br\cdot CONH_2$.—This is readily obtained by the action of strong aqueous ammonia on the chloride; it separates from boiling water in glistening plates which melt at 151°. (See Engler, *Ber*, 1871, **4**, 708.)

Parabromobenzoyl Chloride [COCl : Br = 1 : 4]

Jackson and Rolfe (*Amer. Chem. J.*, 1887, **9**, 85) have prepared this chloride by a somewhat tedious process. They describe it as crystallising in needles which melt at 30°, and distil, under atmospheric pressure, at 245—247°, at the same time undergoing partial decomposition. The chloride has also been prepared by Schotten (*Ber.*, 1888, **21**, 2249), who describes it as crystallising in needles which melt at 42°.

The simplest method for the preparation of the chloride is to heat the finely divided parabromobenzoic acid with the requisite quantity of phosphorus pentachloride, and then to distil under diminished pressure. After all the phosphorus oxychloride has passed over, the temperature rises rapidly, and the bromobenzoyl chloride distils over at 154—155° under a pressure of 50 mm. On cooling, it sets to a mass of minute needles which melt at 39—40°. It is readily soluble in all organic solvents, and may with some difficulty be recrystallised from light petroleum (b. p. 40—60°); it forms colourless, prismatic needles melting at 41°.

It has the characteristic penetrating odour, and is remarkably volatile with steam, but is at the same time decomposed. It is only slowly acted on by cold water.

Decomposition with Boiling Water.—

	Chloride.	Water	Time	AgCl	Per cent. decomposed.
(1)	0·5 gr	20 c.c.	2 mins.	0·1500 gr.	45·88
(2)	0·5 „	20 „	4 „	0·2940 „	89·94
(3)	0·5 „	20 „	6 „	0·3250 „	99·42

Decomposition with Sodium Hydroxide Solution.—Half a gram of the chloride, heated with 20 c.c. of the 8 per cent. soda solution, was completely decomposed by the time the solution boiled; on acidifying, parabromobenzoic acid melting at 252° was thrown down.

Methylic Salt $C_6H_4Br\cdot COOCH_3$.—Hot methylic alcohol acts vigorously on the chloride, and the methylic salt thus formed separate from its alcoholic solution in large, glistening, prismatic plates which melt at 78° Olgiati (*Ber*, 1894, **27**, 3396), who has quite recently prepared it from the silver salt and methylic iodide, gives the melting point at 74°, whereas Rupe (*Ber.*, 1895, **28**, 260), who also obtained it from the silver salt, states that it melts at 81°. As such different melting points are given by different authorities, I have prepared the ethereal salt by saturating a solution of the acid in methylic alcohol with dry hydrogen chloride, and have found it to agree in every respect with the salt obtained from the acid chloride. Prepared by either method, it forms well-developed, glistening, prismatic plates, which melt sharply at 78°.

Amide, $C_6H_4Br{\cdot}CONH_2$ —This is readily prepared by the action of strong aqueous ammonia on the chloride. The action is very vigorous, and the product crystallises from boiling water in long, colourless needles which melt at 186°. Jackson and Rolfe also give 186° as the melting point.

2 : 4-*Dibromobenzoyl Chloride* [$COCl : Br_2 = 1 : 2 : 4$].

In order to prepare the chloride, the acid (for preparation of acid see following paper) was treated with the requisite quantity of phosphorus pentachloride. After distilling off the oxychloride of phosphorus, the residue was dissolved in light petroleum (b. p. 40—60°), and, on allowing the solution to stand, the dibromobenzoyl chloride separated in long, prismatic needles. On recrystallising from light petroleum, it formed yellowish, hard prisms which melted at 48—49°. The chloride is readily soluble in all organic solvents, and has a slightly acid chloride smell, which is greatly intensified by warming with water. It is to some extent volatile with steam, but is, at the same time, decomposed.

0·300 gave 0·5190 mixed AgCl and AgBr, which, reduced in a stream of hydrogen, gave 0·3235 Ag.

	Theory.	Found.
Br........	53·60 per cent.	53·43 per cent.
Cl........	11·89 „	11·74 „

Decomposition with Sodium Hydroxide Solution—Half a gram of the acid chloride when boiled with 20 c.c. of the alkali solution was completely decomposed within three minutes. The amount of hydrogen chloride formed was estimated after the boiling had been continued for 1½ minutes.

0·5 chloride gave 0·2264 AgCl; equivalent to 94·19 per cent. decomposed. The acid, which was recovered, melted at 167°.

Methylic Salt, $C_6H_3Br_2{\cdot}COOCH_3$.—This was readily obtained by boiling the chloride for a few minutes with methylic alcohol; on standing, it separates out as an oil, which solidifies to a mass of small needles when kept for some time in a desiccator over sulphuric acid. These, when recrystallised from chloroform, melt at 33°, and agree in every respect with the product obtained directly from the acid. It is very difficult to obtain pure, as it is so readily soluble in all organic solvents.

3 : 5-*Dibromobenzoyl Chloride* [$COCl : Br_2 = 1 : 3 : 5$].

The 3 : 5-dibromobenzoic acid was prepared from the dibromoparamido-acid, which is readily obtained by the action of bromine water on paramidobenzoic acid.

Forty grams of the finely divided dibromamido-acid were suspended in 150 c.c. of absolute alcohol, and the whole heated on the water bath in a flask connected with a reflux condenser; nitrous fumes (from white arsenic and nitric acid) were then passed into the boiling mixture until all the dibromamido-acid had disappeared, and a clear solution was formed. This was diluted with cold water, and the dibromobenzoic acid, which was thrown down in the form of small needles, was collected, dissolved in dilute sodium carbonate solution, and boiled for some time with animal charcoal. On acidifying the alkaline solution with hydrochloric acid, pure 3 : 5-dibromobenzoic acid was obtained, melting at 209°; the yield was a little over 50 per cent. of the theoretical.

The chloride was prepared in the same way as the 2 : 4-derivative. It distilled at 189° under a pressure of 45 mm. On cooling, it solidified to a mass of small, colourless needles melting at 41°. It is very readily soluble in all organic solvents, but may be recrystallised from light petroleum (b. p. 40—60°).

This chloride is scarcely acted on by cold water, and only slowly by boiling water. Half a gram of the chloride was completely decomposed on boiling for 40 minutes with 20 c.c. of distilled water. It has a faint acid chloride smell, which is greatly intensified by warming with water.

0·3010 gave 3·5220 mixed AgCl and AgBr, which, when reduced, gave 0·3256 Ag.

	Theory.	Found.
Br........	53·60 per cent.	53·37 per cent.
Cl........	11·89 ,,	11·87 ,,

Decomposition with Sodium Hydroxide Solution.—Half a gram of the chloride and 20 c.c. of the 8 per cent. soda solution were heated on the sand bath; the chloride was entirely decomposed by the time the solution began to boil. The acid recovered from the alkaline solution melted at 209°.

Methylic Salt, $C_6H_3Br_2\cdot COOCH_3$.—As obtained from the chloride, this agreed in all respects with that prepared by saturating a methylic alcoholic solution of the acid with hydrogen chloride. It separates from its alcoholic solution in prismatic needles, which melt at 63°, and are readily soluble in ether, alcohol, and benzene.

Amide, $C_6H_3Br_2\cdot COOH$.—This was formed by the action of aqueous ammonia on the chloride. It crystallises from dilute alcohol in glistening plates melting at 187°.

2 : 6-*Dibromobenzoyl Chloride* [COCl : Br_2 = 1 : 2 : 6].

After heating the acid with the requisite quantity of phosphorus pentachloride and distilling off the oxychloride, the residue was treated with water, extracted with ether, the ethereal solution shaken out with dilute sodium carbonate and the ether evaporated. The oil which remained was dissolved in light petroleum (b. p. 40—60°) and the solution allowed to stand, when the chloride separated in the form of large, prismatic plates which, after recrystallisation from light petroleum, melted at 46°. The chloride is readily soluble in all organic solvents, has no odour, and is very stable towards cold water, but when boiled with it is decomposed within 30 minutes.

0·200 gave 0·3510 mixed AgCl and AgBr, which, when reduced, gave 0·2190 Ag.

	Theory.	Found.
Br........	53·60 per cent.	53·94 per cent.
Cl........	11·89 ,,	12·06 ,,

Decomposition with Sodium Hydroxide Solution.—This acid chloride, when heated with the 8 per cent. soda solution, proved to be much more stable than any of the chlorides previously mentioned. The following numbers were obtained—

(1) 0·5 gram of chloride was boiled with 20 c.c. of the alkali solution for five minutes. A residue of 0·4010 gram of unaltered chloride was obtained = 19·80 per cent. decomposed; and 0·0470 gram AgCl was obtained from the filtrate = 19·56 per cent. decomposed. Mean = 19·68 per cent.

(2) The same quantities were boiled for 10 minutes when a residue of 0·313 gram was obtained = 37·40 per cent. decomposed; and 0·0890 gram AgCl was obtained from the filtrate = 37·03 per cent. Mean = 37·21 per cent.

(3) On boiling for 20 minutes, a residue of 0·1530 gram of unaltered chloride was obtained = 69·40 per cent. decomposed, and 0·1650 gram AgCl was formed from the filtrate = 68·64 per cent. Mean = 69·02 per cent.

(4) 0·5 gram of the acid chloride, when boiled with 20 c.c. of the soda solution, was entirely decomposed after 35 minutes. A minute quantity of an insoluble residue was left, but this was far too small for further investigation.

Methylic Salt, $C_6H_3Br_2 \cdot COOCH_3$.—This was obtained by boiling the acid chloride with excess of methylic alcohol for half an hour. It is readily soluble in alcohol, ether, and even in light petroleum (b. p. 40—60°). It crystallises from alcohol in colourless, glistening plates which melt at 78°. Prepared by treating the silver salt of the acid with methylic iodide, it melted at 78° and corresponded in all respects with the above.

0·2125 gave 0·2696 AgBr. Br = 53·99.

Theory requires Br = 54·42 per cent.

Amide, $C_6H_3Br_2 \cdot CONH_2$.—This was obtained from the nitrile as an intermediate product in the formation of the acid, and also by the action of aqueous ammonia on the chloride. It is soluble in boiling water, from which it crystallises in hard prismatic needles; these begin to soften at 186° and melt at 192°.

3 : 4 : 5-*Tribromobenzoyl Chloride* [COCl : Br_3 = 1 : 3 : 4 : 5].

This acid was prepared from dibromoparamidobenzoic acid by replacing the amido-group by bromine (Sudborough, *Ber.*, 1894, **27**, 512).

In order to obtain a good yield, it is necessary to use a large excess of sodium nitrite, and not to keep the temperature too low during the diazotizing. The diazo-solution should be added to the hot cuprous bromide solution, as then no trace of tarry matter is formed; after heating for half an hour on the water bath, the solution is filtered and the residue extracted with cold alcohol, in which the tribromo-acid is readily soluble; it may be obtained from its alcoholic solution by adding water, when it separates in minute needles. After recrystallisation from dilute alcohol or hot benzene, the acid forms long, colourless needles which melt at 235°.

In order to prepare the chloride, the acid is well mixed with the requisite quantity of phosphorus pentachloride in a mortar, and the mixture is heated in a small flask; if the two are not well mixed, a considerable quantity of an insoluble product is formed (probably the anhydride). After distilling off the oxychloride, the residue is extracted with hot light petroleum (b p. 40—60°); the acid chloride separates from this solution in clusters of small yellowish needles, which, after recrystallisation, melt at 83°. The chloride has no odour, and is only slowly decomposed by boiling water.

0·200 gave 0·372 mixed AgCl and AgBr* which on reduction gave 0·227 Ag.

	Theory.	Found.
Br........	63·57 per cent.	63 26 per cent.
Cl........	9·40 „	9·23 „

Decomposition with Sodium Hydroxide Solution.—Half a gram of the chloride was heated on the sand bath with 20 c.c. of the alkali solution; the whole was decomposed by the time the solution began to boil. On acidifying the solution of the sodium salt with hydrochloric acid, it yielded the 3 : 4 : 5-tribromo-acid melting at 235°. It may be noted that the sodium salt of this acid is only sparingly soluble in cold water.

Methylic Salt, $C_6H_2Br_3{\cdot}COOCH_3$.—This was obtained direct from the acid, and also by boiling the chloride for a few minutes with methylic alcohol. It is somewhat sparingly soluble in alcohol, from which it separates in long needles melting at 154°.

The ethylic salt, $C_6H_2Br_3{\cdot}COOC_2H_5$, which was prepared by heating the chloride with ethylic alcohol, crystallises in prismatic needles melting at 126°.

Amide, $C_6H_2Br_3{\cdot}CONH_2$.—The amide, obtained by the action of aqueous ammonia on the chloride, was recrystallised from dilute alcohol, when it was obtained in small needles melting at 210°.

2 : 4 : 6-*Tribromobenzoyl Chloride* [$COCl : Br_3 = 1 : 2 : 4 : 6$].

The tribromobenzoic acid was obtained from the tribromometamido-acid by the elimination of the amido-group by means of ethylic nitrite as recommended by Volbrecht (*Ber.*, 1877, **10**, 1708). The method adopted was similar to that used in the preparation of the 3 : 5-dibromo-acid. In order to purify the acid, it was boiled in benzene solution with animal charcoal; it crystallised from benzene in small hard needles which melt at 187°. This method was found more convenient for the preparation of large quantities of the acid than that formerly given by the author (*Ber.*, 1894, **27**, 512).

The chloride was readily prepared by heating together the requisite quantities of acid and phosphorus pentachloride. After distilling off the phosphorus oxychloride under diminished pressure, the residue was recrystallised several times from light petroleum (b. p. 40—60°). It forms large, colourless, prismatic plates, some of which are nearly cubes; these are readily soluble in all organic solvents, and melt at 47°. This chloride does not possess the penetrating acid chloride smell; it is remarkably volatile with steam, and is only slowly decomposed by boiling water. After boiling for 30 minutes, only 28 per cent. was decomposed.

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* In order to completely decompose the organic matter, it is necessary to heat for several hours at 300—320° in the sealed tube.

0·200 gave 0·373 mixed AgCl and AgBr which on reduction gave 0·2275 Ag.

	Theory.	Found.
Br........	63·57 per cent.	63·56 per cent.
Cl........	9·40 „	9·18 „

Decomposition with Sodium Hydroxide Solution.—

(1) 0·5 gram was boiled with 20 c.c. of the solution for 30 minutes. A residue of 0·358 gram of unaltered chloride was obtained (= 28·40 per cent. decomposed); and the filtrate yielded 0·0535 gram AgCl, = 28·14 per cent. decomposed. Mean = 28·27 per cent.

(2) A second experiment gave mean = 30·18 per cent.

(3) After boiling for 60 minutes, 0·5 gram gave 0·240 gram of unaltered chloride = 52·00 per cent. decomposed, and 0·1020 gram AgCl = 55·66 per cent. Mean = 52·83 per cent.

(4) After 90 minutes 0·5 gram gave 0·0966 gram of unaltered chloride = 80·68 per cent. decomposed, and 0·1550 gram AgCl = 81·55 per cent. Mean = 81·11 per cent.

The decomposition was more rapid when the chloride was boiled with the alkali solution over the free flame instead of on the sand bath; in this way, complete decomposition could be brought about in 45 minutes.

The recovered acid melted at 187°, and the chloride at 46°.

Methylic Salt, $C_6H_2Br_3\cdot COOCH_3$.—This was obtained by boiling the chloride for some time with methylic alcohol. It is very soluble in all organic solvents, and separates from its alcoholic solution in the form of needles melting at 67°.

0·2466 gram gave 0·3730 gram AgBr.

	Theory.	Found.
Br........	64·34 per cent.	64·37 per cent.

It was also prepared by the action of methylic iodide on the silver salt of the acid. It agreed in all respects with the above.

Amide, $C_6H_2Br_3\cdot CONH_2$.—Cold aqueous ammonia does not react with the acid chloride; but on heating the two together for some minutes the amide is readily formed. When recrystallised from dilute alcohol, it forms slender colourless needles which melt at 193°.

2 : 3 : 4 : 6-*Tetrabromobenzoyl Chloride* [$COCl : Br_4 = 1 : 2 : 3 : 4 : 6$].

The acid was obtained by the method given by Meyer and Sudborough (*Ber.*, 1894, **27**, 1583); it is only necessary to add that excess of sodium nitrite need not be used, as the tribromamido-acid is readily diazotised; and also that it is better to run the diazo-solution into the cold cuprous bromide, as otherwise tarry matter is readily formed.

The acid was purified by boiling in benzene solution with animal charcoal. After several recrystallisations, it was obtained in small colourless needles melting at 179°.

0·2230 gave 0·0160 H_2O and 0·1624 CO_2. C = 19·86; H = 0·79.
0·2402 „ 0·0178 „ 0·1690 CO_2. C = 19·18; H = 0·82.
0·2005 „ 0·3425 AgBr. Br = 72·70.
Theory requires C = 19·18; H = 0·45; Br = 73 06 per cent.

The chloride, prepared in the same way as the 2 : 4 : 6-derivative, formed fine, somewhat discoloured needles, which, after further purification by boiling for 15—20 minutes with soda solution and recrystallisation from light petroleum, separated in colourless prisms, almost cubes, and melted at 58°.

This chloride is remarkably stable both towards boiling water and caustic alkali; it was not completely decomposed when boiled with water for 1½ hours. It is quite odourless, and is soluble in ether, benzene, light petroleum, and hot alcohol, but only slightly so in cold alcohol.

(1) 0·200 gave 0·3884 mixed AgCl and AgBr which when reduced gave 0·2340 Ag.
(2) 0·250 gave 0·4860 mixed AgCl and AgBr which when reduced gave 0·2924 Ag.

	Theory.	Found. I.	Found. II.
Br	70·09 per cent.	69·65	70·10 per cent.
Cl	7·77 „	7·55	7·34 „

Decomposition with Sodium Hydroxide Solution.—

(1) 0 5 gram of the chloride was boiled with 20 c.c. of the 8 per cent. solution for an hour on the sand bath. A residue of 0·4680 gram of unaltered chloride was obtained, and the filtrate gave only a very small quantity of silver chloride. Decomposition = 6·4 per cent.
(2) The above was repeated. A residue of 0·4600 gram of unaltered chloride was obtained. Decomposition = 8 0 per cent.

The decomposition was more rapid when the mixture was heated over wire gauze, or over a free flame. The recovered acid was found to melt at 179°.

Methylic Salt, $C_6HBr_4\cdot COOCH_3$.—This was obtained from the silver salt and methylic iodide; after recrystallisation from alcohol, it forms clusters of hard, prismatic needles, which melt at 77°.

0·2670 gave 0·4420 AgBr. Br = 70·44.
Theory requires Br = 70·79 per cent.

Attempts made to prepare this ethereal salt by the action of methylic alcohol on the chloride were unsuccessful; the chloride disappeared after boiling the mixture for some time, but, on allowing it to stand, an oil separated, which did not solidify when kept for some time over sulphuric acid, and gave most of the reactions for the chloride.

2 : 6-*Dinitrobenzoyl Chloride* [$COCl : (NO_2)_2 = 1 : 2 : 6$].

The diorthonitrobenzoic acid was prepared by Benfey's method (*Ber.*, 1894, **27**, 3148) from pure 2 : 6-dinitrotoluene, which Professor Meyer was kind enough to send me. It forms colourless needles, which dissolve readily in water and melt at 202°. The chloride was obtained by the action of phosphorus pentachloride on the acid; it is necessary that the two should be well mixed, as otherwise a quantity of the anhydride is formed. After distilling off most of the phosphorus oxychloride, the residue was treated with cold water, allowed to stand a short time, and then extracted with ether. The ethereal solution, after shaking out with dilute sodium carbonate solution and drying over calcium chloride, was allowed to evaporate, and the chloride was thus obtained in the form of yellowish plates, which melted at 98°.

0·200 gave 0·125 AgCl. Cl = 15·46.
0·220 „ 23·3 c.c. moist nitrogen at 15° and 758 mm. N = 12·37.
Theory requires Cl = 15·40; N = 12·14 per cent.

The chloride is odourless and is not decomposed by cold water, but when boiled with it, is slowly decomposed. 0·5 gram boiled with 20 c.c. water for 30 minutes gave 0·305 gram AgCl, equivalent to 97·98 per cent. decomposed.

The decomposition with sodium hydroxide could not be followed out, as other actions occur simultaneously. Thus, on warming with caustic alkali, the chloride dissolves, forming a deep red solution, similar to that given by the acid when treated with excess of alkali.

Methylic Salt, $C_6H_3(NO_2)_2COOCH_3$.—This was obtained by boiling the chloride with methylic alcohol. It crystallises in glistening plates, which are soluble in boiling alcohol but not in cold; it melts at 147°, and gives a deep red colour with caustic soda.

0·261 gave 27 c.c. moist nitrogen at 15° and 768 mm. N = 12·24.
Theory requires N = 12·38 per cent.

2 : 4 : 6-*Trinitrobenzoyl Chloride* [$COCl : (NO_2)_3 = 1 : 2 : 4 : 6$].

The trinitrobenzoic acid was kindly presented to me by the "Chemische Fabrik Griesheim." To prepare the chloride, the acid must be intimately mixed with the requisite quantity of phosphorus pentachloride and then heated; it is advisable not to distil off all the oxychloride, as an explosion ensues if the residue is overheated. To separate the acid chloride from the oxychloride, the mixture is pressed on a porous plate, and finally recrystallised from benzene; on cooling, the chloride separates in well-developed plates, apparently containing benzene of crystallisation, as they effloresce when exposed to the air. The powder thus formed melts at 158°.

0·300 gave 0 1493 AgCl. Cl = 12·32.
0·2184 " 29·4 c.c. moist nitrogen at 16° and 755 mm. N = 15·58.
Theory requires Cl = 12·88; N = 15·24 per cent.

The chloride is very stable towards boiling water (see Meyer, *Ber.*, 1894, **27**, 3153), but is at once dissolved on warming with sodium hydroxide, forming a deep red solution. It is only sparingly soluble in ether, and insoluble in light petroleum.

If a mixture of pentachloride and oxychloride of phosphorus is used in the preparation of the chloride, as recommended by V. Meyer, a quantity of anhydride is formed; this crystallises in small, colourless needles, insoluble in ether or alcohol, and only slightly soluble in benzene. They melt at 270°, and, at the same time, undergo decomposition.

0·172 gave 24·9 c.c. moist nitrogen at 14° and 756 mm. N = 16·94.
Theory requires N = 16 94 per cent.

Methylic Salt, $C_6H_2(NO_2)_3{\cdot}COOCH_3$.—This was obtained by boiling the chloride with a very large excess of methylic alcohol for some time, also by the action of methylic iodide on the silver salt of the acid. As prepared by either method, it forms yellowish, prismatic plates, which melt at 157°, and are only soluble in alcohol and ether with difficulty.

Ethylic Salt, $C_6H_2(NO_2)_3{\cdot}COOC_2H_5$.—This was obtained by the action of ethylic alcohol on the chloride, and by heating the silver salt of the acid with excess of ethylic iodide. It forms yellowish plates, sparingly soluble in alcohol and ether, and melts at 155°.

0·1722 gave 21·8 c.c. moist nitrogen at 15° and 762 mm. N = 14·86.
Theory requires N = 14·73 per cent.

Both the ethereal salts dissolve in alkali solutions when gently warmed, yielding deep red solutions.

CONCLUSION.

The results recorded in the preceding pages show—

1. That the acid chlorides in which substitution does not occur in either of the ortho-positions are readily decomposed by dilute alkalis, the decomposition being almost instantaneous at the boiling point of the alkali solution.

2. That the acid chlorides which have a bromine atom in one ortho-position are relatively more stable towards alkalis. Thus, orthobromo- and 2 : 4-dibromo-benzoyl chloride are completely decomposed after boiling with the alkali solution for two to three minutes.

3. That acid chlorides, in which both ortho-positions are occupied by bromine atoms, are remarkably stable, and are only converted into the corresponding sodium salts of the acids by long-continued boiling with an alkali solution.

If substitution has already taken place in the two ortho-positions with respect to the COCl group, the introduction of bromine atoms into the benzene nucleus seems to render the acid chloride still more stable.

These results are interesting when compared with those recently obtained by V. Meyer on the hydrolysis of the ethereal salts of substituted benzoic acids. Professor Meyer informs me he has found that the ethereal salts of monortho-substituted benzoic acids are somewhat more stable towards hydrolysing agents than their isomerides, and are also formed more slowly. Further, that the corresponding diortho-substituted derivatives exhibit the same stability towards hydrolysing agents, but in a more marked degree.

LXV.—*Diortho-substituted Benzoic Acids.* II. *Hydrolysis of Aromatic Nitriles and Acid-amides.*

By J. J. SUDBOROUGH.

AT present there appears to be no good general method by which considerable quantities of aromatic acids can be obtained from the corresponding nitriles.

The following are the methods most usually adopted.

1. Hydrolysis by heating with excess of concentrated hydrochloric acid at 200—230°. This method is of very general application and gives good results, but as it necessitates the use of sealed tubes, only small quantities of acid can be prepared by this method.

2. Hydrolysis with alcoholic potash. This gives good results in many instances, but in others secondary actions occur, especially in the case of nitriles containing one or more nitro-groups.

3. Hydrolysis by boiling with moderately concentrated (50—70 per cent.) sulphuric acid. Large quantities of the nitrile can be treated in this way, but in many instances the action proceeds no further than the formation of the acid amide (see Claus, *Annalen*, 265, 266, 269).

4. Bouveault's method (*Bull. Soc. Chim*, [3], 1892, 9, 368), by which the nitrile is converted into the acid amide and then treated with sodium nitrite. According to Bouveault, this method can only be employed for those nitriles which yield the corresponding acid amides when heated on the water bath for several hours with 90 per cent. sulphuric acid.

By a slight modification of Bouveault's method, it has been found possible not only to render it of far more general application but also to shorten the time required for the operation.

Bouveault's method as thus modified is as follows.

The purified nitrile is heated with 25—30 times its weight of 90 per cent. sulphuric acid at 120—130° either on a sand bath or in an oil bath for about an hour.* By this means the nitrile is converted into the acid amide, and the clear, slightly coloured, solution is allowed to cool and then treated with the theoretical quantity of sodium nitrite dissolved in as little water as possible.

In this operation it is necessary to keep the solution at about 20—30°, to run in the sodium nitrite under the surface of the sulphuric acid by means of a separating funnel, and to stir vigorously the whole time. If these precautions are taken, no evolution of gas occurs. The mixture, which is now dark red, is gently warmed on the water bath until evolution of gas ceases. A capacious flask should be used as the evolution of gas is sometimes tumultuous. On pouring the mixture into cold water the acid, mixed with a little amide, is thrown down and may be purified by dissolving it in a solution of sodium carbonate and re-precipitating with hydrochloric acid.

The following acids have been obtained by this method:—Parabromobenzoic acid, 2:4-dibromobenzoic acid, 2:6-dibromobenzoic acid, 2:4:6-trichlorobenzoic acid.

The yield of acid is very good and the method would appear to be of special use for the hydrolysis of nitriles containing nitro-groups and of diortho-substituted nitriles, both of which are difficult to hydrolyse by the other methods.

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* This large excess of sulphuric acid is necessary, as, otherwise, part of the acid amide separates out on cooling.

2 : 6-*Dibromobenzoic acid* [COOH : Br_2 = 1 : 2 : 6].

As this acid is soluble in cold water to a considerable extent, it is necessary in its preparation to extract the sulphuric acid mixture with ether, and then shake out with a solution of sodium carbonate. When recrystallised from hot water in which it is readily soluble, it separates in long needles or short prisms which melt at 146·5°. Claus and Weil give 189° as the melting point, but according to a recent communication, Claus makes it 146°. The acid is readily soluble in ether, alcohol, chloroform and hot water. Although its melting point is so much above 100°, the acid melts when heated with water, and also separates out as an oil from its hot concentrated aqueous solutions. The following were the results of analyses:—

	Theory.	Found.
C........	30·00 per cent.	30·13 per cent.
H	1·43 „	1·66 „
Br	57·14 „	56·90 and 57·03 „

2 : 6-*Dibromobenzamide*, $C_6H_3Br_2 \cdot CONH_2$.—This compound was obtained as an intermediate product in the preparation of the acid from the nitrile. It crystallises from hot water, in hard prismatic needles which melt at 192°.

	Theory.	Found.
N	5·01 per cent.	5·02 per cent.

This amide is characterised by its great stability towards hydrolysing agents. When heated with excess of 80 per cent. sulphuric acid at 170° for several hours in a sealed tube, not a trace of the acid was formed, and the amide was recovered unaltered.

2 : 4-*Dibromobenzamide*, $C_6H_3Br_2 \cdot CONH_2$.

This compound prepared from the nitrile and also from the acid chloride is much less soluble in hot water than the diortho-compound. It crystallises from hot dilute alcohol in long needles which melt at 195°, and are only slightly soluble in ether.

	Theory.	Found.
N	5·01 per cent.	5·21 per cent.

This amide differs from the 2 : 6-derivative in the readiness with which it can be converted into the corresponding acid. When heated for six hours at 170° with excess of 80 per cent. sulphuric acid, it is entirely converted into the 2 : 4-dibrom-acid, whereas the diortho-amide gives no trace of acid under the same condition.

The remarkable stability of the diortho-substituted benzoyl chlorides taken together with the behaviour of 2 : 6-dibromobenzamide towards sulphuric acid suggests the conclusion that diortho-substituted benzamides as a rule are very stable and are much more difficult to hydrolyse than their isomerides.

A perusal of the researches of Claus and his pupils (*J. pr. Chem.*, 1888, [2], **37**, 197; *Annalen*, vols. **265**, **266**, **269**, **274**) on the hydrolysis of various aromatic nitriles shows that this conclusion is supported by most of their results. Their experiments show that whilst most nitriles are hydrolysed to the corresponding acids by boiling for several hours with 60—70 per cent. sulphuric acid, those nitriles in which substitution occurs in the two ortho-positions yield the acid amide and not the acid under the same conditions.

Two important exceptions appear to be the 2 : 6-dichlorobenzonitrile and the 2 : 4 : 6-methyl-chloronitrobenzonitrile According to Claus and Stavenhagen (*Ann.*, 1892, **269**, 228) the 2 : 6-dichlorobenzonitrile is directly converted into the corresponding acid when heated with sulphuric acid in sealed tubes at 150°, and according to Claus and Stapelberg (*Ann.*, 1893, **274**, 298) the 2 : 4 : 6-methylchloronitrobenzonitrile yields the acid when vigorously boiled for 10 hours with 60 per cent. sulphuric acid.

The behaviour of the 2 : 6-dichloronitrile appears remarkable when compared with the great stability of the corresponding dibromobenzamide, and it is my intention to quantitatively follow the hydrolysis of various bromo- and chloro-substituted benzamides, in order to see whether the diortho-compounds are in all cases more difficult to hydrolyse than their isomerides.

LXVI.—*Note on the Action of Sodium Ethoxide on Deoxybenzoïn.*

By J. J. SUDBOROUGH.

IN attempting to prepare various substituted derivatives of deoxybenzoïn, $C_6H_5\cdot CO\cdot CH_2\cdot C_6H_5$, by heating mixtures of deoxybenzoïn with sodium ethoxide and various halogen compounds, a quantity of stilbene, $C_6H_5\cdot CH{:}CH\cdot C_6H_5$, was always obtained as one of the products. Further experiments have shown that deoxybenzoin when heated with sodium ethoxide alone at 170°, in sealed tubes, is partially converted into stilbene. Five grams of the ketone were heated with the equivalent quantity of sodium ethoxide at 170° during 3—4 hours. When cool, the contents were poured into water, and after the oil which was thus thrown down had solidified, it was dissolved in hot alcohol; on cooling, the stilbene separated in large, glistening, slightly fluorescent plates melting at 125°.

	Theory.	Found.
C........	93 33 per cent.	93·20 per cent.
H........	6·66 „	7·14 „

From 40—50 per cent. of the deoxybenzoïn was thus obtained as stilbene. The mother liquor from the stilbene, when concentrated, yielded an oil which solidified on cooling, and melted at about 60°. This, on recrystallisation from hot light petroleum (b. p. 40—50°), separated in long, glistening, prismatic needles, which melted at 63°. It is readily soluble in ether, alcohol, chloroform, and hot light petroleum. Analysis proved it to be hydroxydibenzyl,

$$C_6H_5{\cdot}CH(OH){\cdot}CH_2{\cdot}C_6H_5,$$

the so-called stilbene hydrate.

	Theory	Found.
C........	84·84 per cent.	84·91 per cent.
H	7·07 „	6·86 „

This compound has previously been obtained by Limpricht and Schwanert (*Annalen*, 1870, **155**, 62), by the reduction of deoxybenzoïn with sodium amalgam. It is characterised by the readiness with which it loses the elements of water, and is converted into stilbene.

$$C_6H_5{\cdot}CH(OH){\cdot}CH_2{\cdot}C_6H_5 = C_6H_5{\cdot}CH{:}CH{\cdot}C_6H_5 + H_2O.$$

When distilled under atmospheric pressure, an oil passed over between 290° and 310°; this solidified on cooling, and proved to be stilbene itself. The hydroxy-derivative also loses water when heated with dilute sulphuric acid.

From these facts it is evident that the hydroxydibenzyl is first produced by the reducing action of the sodium ethoxide, and that this is afterwards converted into stilbene by the loss of water.

Experiments were also made by heating deoxybenzoïn with sodium methoxide, but not a trace of stilbene was formed. This is interesting when compared with the results obtained by Lobry de Bruyn on the action of sodium methoxide and ethoxide on various aromatic nitro-derivatives.

De Bruyn has shown that whilst sodium methoxide merely acts as a substituting agent, displacing a nitro- by a methoxy-group, the ethoxide under the same circumstances also acts as a reducing agent, producing more or less of the corresponding azo-compounds. It would thus appear that sodium methoxide is much to be preferred to the ethoxide if it is desired to prevent reduction taking place.

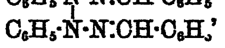
LXVII.—*Stereoisomeric Osazones.* Part I.

By Harry Ingle, Ph.D., B.Sc., and Harold H. Mann, B.Sc.

According to the theory of nitrogen isomerism proposed by Hantzsch and Werner, just as the 1 : 2-dioximes exist in several modifications, so also should the 1 : 2-dihydrazones or osazones show a similar isomerism. Anschütz and Pauly (*Ber*, 1895, **28**, 64) have, in fact, quite recently succeeded in preparing the three theoretically possible forms of the osazone of dihydroxytartaric acid. With this exception, however, all attempts to obtain the various modifications of these substances have proved futile, the methods invariably leading to one and the same dihydrazone.

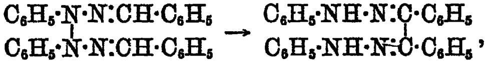
The osazone of benzile, being one of the easiest to prepare, has been the object of attack by several chemists. Auwers and his scholars (*Ber.*, **26**, 788; **27**, 1133), especially, have tried to obtain such stereoisomerides by the use of substituted hydrazines, and Smith and Ransom (*Amer. Chem. J.*, 1894, **16**, 115) have heated the stereoisomeric hydrazones of benzoïn with phenylhydrazine in acetic acid solution. In all cases, however, only one modification could be isolated.

In continuation of an investigation on the derivatives of tetrazole, we had occasion to study the action of iodine on a mixture of sodium ethoxide and benzalphenylhydrazone. The fact that alkylogens enter into reaction with the sodium derivative of this last-named compound was first noticed by B. Philips (*Ber.*, 1887, **20**, 2485), but the substitution of sodium alcoholates for sodium in similar reactions was first made by Landsberg (*vide* Japp and Klingemann, Trans., 1888, **53**, 519). The application of Landsberg's modification of Philip's method to benzalphenylhydrazone does not appear to have been studied.

By the interaction of an ethereal solution of iodine with a mixture of sodium ethoxide and benzalphenylhydrazone, also dissolved in ether, and all in molecular proportion, the formation of a compound,  $\begin{array}{l} C_6H_5\cdot N\cdot N{:}CH\cdot C_6H_5 \\ \qquad\;\, | \\ C_6H_5\cdot N\cdot N{:}CH\cdot C_6H_5 \end{array}$, was to be expected. On carrying out the experiment we found that two well-defined crystalline substances were formed, melting at 208° and 186° respectively, the former in much the larger quantity. On analysis it was found that both had the formula $(C_{13}H_{11}N_2)_x$.

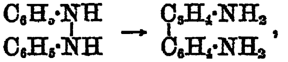
At this point it came to our knowledge that v. Pechmann (*Ber.*, 1893, **26**, 1045) had obtained a compound of the same composition by direct oxidation of benzalphenylhydrazone with amylic nitrite. The same substance had previously been obtained by Minunni (*Gazzetta*, 1892, **22**, ii, 217), using mercuric oxide as the oxidising agent.* v. Pechmann assigned the constitutional formula above suggested to this compound, and named it dibenzaldiphenylhydrotetrazone (*Ber.*, 1894, **27**, 2920). On repeating the experiments of these two chemists, we found that in both cases the same substance was formed, and that it was identical with the compound melting at 186°, previously obtained by the action of iodine on sodium benzalphenylhydrazone.

Thinking that the other substance, melting at 208°, might be obtained by the action of alkali on the hydrotetrazone first produced, we heated the latter, dissolved in benzene, with alcoholic potash, and found, to our surprise, that the compound produced was not the one melting at 208°, but that it melted at 225°, and was in every respect identical with benzileosazone. An intramolecular change has then occurred,



$$\begin{array}{l}C_6H_5\cdot N\cdot N{:}CH\cdot C_6H_5\\ \qquad\ |\\ C_6H_5\cdot N\cdot N{:}CH\cdot C_6H_5\end{array} \rightarrow \begin{array}{l}C_6H_5\cdot NH\cdot N{:}C\cdot C_6H_5\\ \qquad\qquad\qquad |\\ C_6H_5\cdot NH\cdot N{:}C\cdot C_6H_5\end{array},$$

similar to that which takes place when hydrazobenzene is treated with acids,

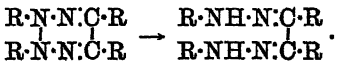


$$\begin{array}{l}C_6H_5\cdot NH\\ \qquad\ |\\ C_6H_5\cdot NH\end{array} \rightarrow \begin{array}{l}C_6H_4\cdot NH_2\\ |\\ C_6H_4\cdot NH_2\end{array},$$

nitrogen linkage giving place to that of carbon.

Just as the rearrangement in the latter case may be viewed as being occasioned by the acid inducing the formation of basic molecules, so in the present instance the presence of alkali determines the formation of acidic imido-groups.

v. Pechmann found that on heating the hydrotetrazone with phenylhydrazine, it suffered reduction to the original benzalphenylhyrazone (*loc. cit.*); we repeated his experiment with the same result, and it appeared of interest to examine the behaviour towards this reagent of the isomeric substance melting at 208°; it was found that partial decomposition took place, and benzileosazone, melting at 225° was formed. According to v. Pechmann, osotetrazones when heated with phenylhydrazine are reduced to the corresponding osazones:



$$\begin{array}{l}R\cdot N\cdot N{:}C\cdot R\\ \quad\ |\qquad\ |\\ R\cdot N\cdot N{:}C\cdot R\end{array} \rightarrow \begin{array}{l}R\cdot NH\cdot N{:}C\cdot R\\ \qquad\qquad\quad\ |\\ R\cdot NH\cdot N{:}C\cdot R\end{array}.$$

The substance under consideration showed, however, none of the reactions of osotetrazones, and the fact that it is very readily oxidised indicates the presence of oxidisable hydrogen.

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* v. Pechmann gives 190° as the melting point of this substance; Minunni 180°. The former also repeated Minunni's experiments, and corrects the melting point given by him. We, however, have not found a higher value than 186° for the substance prepared by any of the three methods.

In order, however, to eliminate the possibility of a mere reduction by the phenylhydrazine, the substance alone was dissolved in ethyl succinate (b. p. 217°), and heated to boiling; it was found that this treatment converted it into benzileosazone. It would appear, especially as the same result was afterwards obtained by heating with ethylic benzoate or malonate, and with alcohol at 200°, that the solvent did not exert any chemical action, but that we had here one of the much sought for stereoisomerides of benzileosazone, which we have named α-benzileosazone.

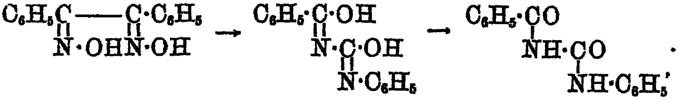
The preparation of osazones directly from aldehydrazones is not new. Japp and Klingemann (Trans., 1888, **53**, 519) have already prepared a number of them by the simple heating of these compounds. Under these conditions, the hydrazone loses hydrogen thus

$$\begin{array}{l} R\cdot CH{:}N\cdot NHR \\ R\cdot CH{:}N\cdot NHR \end{array} = \begin{array}{l} R\cdot C{:}N\cdot NHR \\ R\cdot C{:}N\cdot NHR \end{array} + H_2,$$

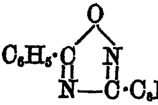
and the dihydrazone of a 1 : 2-diketone is formed. The substances thus obtained do not appear to have differed from those formed by direct condensation of the ketone with hydrazine.

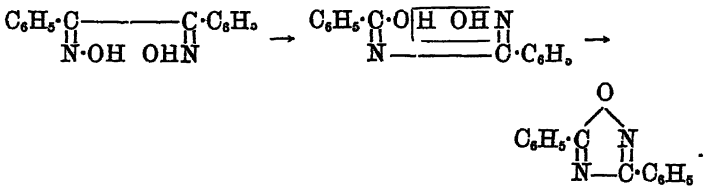
As a means of determining the configuration of the two osazones, we had recourse to the method employed by Hantzsch and Werner, and by Beckmann, in the case of the stereoisomeric oximes. The isomerides, when treated with such agents as sulphuric acid and phosphorus pentachloride, pentoxide, pentasulphide or oxychloride, gave different products, and from a study of these they were led to assign definite space configurations to them.

Of the three compounds derived from benzile, for example, the α and γ varieties gave substances whose formation could only be explained by the severance of the *ketonic carbon linking*, whilst in the case of the β-dioxime this linking remained intact in all the products. The γ-compound yielded benzoylphenylurea, and from experience with the monoximes, the *amphi*-configuration was assigned to this variety. The change was thus represented

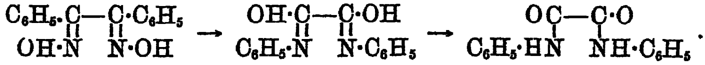


$$\begin{array}{c} C_6H_5C\text{——}C\cdot C_6H_5 \\ \| \qquad \| \\ N\cdot OH\,N\cdot OH \end{array} \rightarrow \begin{array}{c} C_6H_5\cdot C\cdot OH \\ \| \\ N\cdot C\cdot OH \\ \| \\ N\cdot C_6H_5 \end{array} \rightarrow \begin{array}{c} C_6H_5\cdot CO \\ | \\ NH\cdot CO \\ | \\ NH\cdot C_6H_5 \end{array}.$$

The α-variety gave a compound of the formula , dibenzenylazoxime (Gunther, *Annalen*, 1889, **252**, 44), and since it also readily yields an anhydride, the *syn*-configuration was assigned to it. The change would be represented as follows.

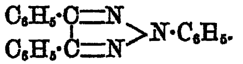


Thirdly, the β-modification gave oxanilide, and may therefore be considered to possess the *anti*-configuration. The reaction may be formulated thus



$$\begin{array}{c}C_6H_5\cdot C{-}C\cdot C_6H_5\\ OH\cdot N\quad N\cdot OH\end{array} \rightarrow \begin{array}{c}OH\cdot C{-}C\cdot OH\\ C_6H_5\cdot N\quad N\cdot C_6H_5\end{array} \rightarrow \begin{array}{c}OC{-}C\cdot O\\ C_6H_5\cdot HN\quad NH\cdot C_6H_5\end{array}.$$

Seeing then that so much information is obtained by the use of these reagents with the dioximes, we determined to study the behaviour of the two benzileosazones towards concentrated sulphuric acid. Each of the osazones after treatment with the cold acid was mixed with water, and the product distilled with steam. Under these conditions the β-modification gave large quantities of benzile, and traces of a substance melting at 115° and crystallising in four-sided flat acute rhombic plates, the nature of which was not determined. The α-variety, on the other hand gave large quantities of benzaldehyde, benzile, and triphenylosotriazole (m. p. 120—121°)



$$\begin{array}{l}C_6H_5\cdot C{=}N\\ C_6H_5\cdot C{=}N\end{array}\!>N\cdot C_6H_5.$$

On rendering the residue in the flask strongly alkaline with caustic potash and again distilling in steam, ammonia, aniline, and some phenylhydrazine were obtained from both modifications.

The production of benzaldehyde from the α-osazone can only be explained by severance of the ketonic carbon linking, and would therefore correspond to the behaviour of the *syn*- and *amphi*-dioximes already cited; the β-variety, yielding no benzaldehyde or allied compound, would be analogous to the *anti*-dioxime.

The formation of triphenylosotriazole corresponds exactly with that of an anhydride by the *syn*-dioxime, and it seems extremely probable that the anilido-groups are nearer in space in this case than in the β-compound.

Auwers and V. Meyer have prepared this osotriazole from ordinary or β-benzileosazone by dry distillation or by heating with alcohol at 210°. The stability of the molecule at the temperature necessary to bring about these reactions, is greatly decreased, and this change cannot therefore be used as an argument in favour of the *syn*-configuration of the ordinary osazone. The action of sulphuric acid is very different. Here the temperature at which the change takes place is one at which both osazones are stable and under these conditions the normal or β-osazone, as already stated, does not yield this osotriazole whereas the α-osazone does.

Anschütz and Pauly (*loc. cit.*) as already mentioned, have recently prepared the stereoisomerides of dihydroxytartaric acid osazone, and on comparing the melting points of these with those of the two benzileosazones a remarkable agreement is noticed.

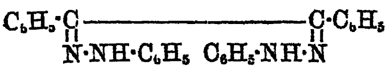
	Osazones of dihydroxytartaric acid.	Benzileosazones.
α-variety............	120—121° C.	207—208° C.
β-variety (most stable)	136—137 "	225° C.
γ-variety............	173—175 "	—

The difference between the melting points of the α and β varieties in the case of the osazones of dihydroxytartaric acid is 16°, and in that of the benzileosazones it is 17°. In each case, the form of the higher melting point is the most stable.

A similar agreement among the monhydrazones and oximes of benzoïn has been noticed by Smith and Ransom (*loc. cit.*).

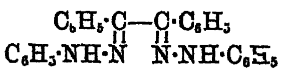
Of the three isomerides prepared by Anschütz and Pauly, the α-compound is attacked by oxidising agents with the formation of a dark violet osotetrazone, while the β- and γ-modifications are unaffected. Thus, since the α-compound most easily yields a ring, it is probably a *syn*-osazone. Of the stereoisomerides of benzileosazone, the α-modification is the more readily oxidisable, yielding, for example, a dark red coloration with potassium dichromate in acetic acid solution; the β-osazone does not yield this coloration. The oxidation products are still under examination.

Finally, therefore, the constitution of the two osazones, as based on the arguments we have adduced would be represented by the following formulæ.



$$\begin{matrix} C_6H_5\cdot C & \text{————————} & C\cdot C_6H_5 \\ \| & & \| \\ N\cdot NH\cdot C_6H_5 & & C_6H_5\cdot NH\cdot N \end{matrix}$$

α-Benzileosazone,
or benzile-*syn*-osazone,
m. p. 208° C.



$$\begin{matrix} C_6H_5\cdot C & — & C\cdot C_6H_5 \\ \| & & \| \\ C_6H_5\cdot NH\cdot N & & N\cdot NH\cdot C_6H_5 \end{matrix}$$

β-Benzileosazone,
or benzile-*anti*-osazone,
m. p. 225° C.

EXPERIMENTAL.

Action of Iodine and Sodium Ethoxide on Benzalphenylhydrazone.

Ten grams of benzalphenylhydrazone were dissolved in ether, to this a solution of 1·4 grams of sodium in 20 c.c. of alcohol was added, and an ethereal solution of 6·5 grams of iodine gradually run in, the mixture being shaken from time to time; sodium iodide at once separated, and the liquid became intensely red. On adding water, the sodium iodide dissolved, and the last traces of iodine were removed by shaking with sodium sulphite solution. On evaporating the ether, a brownish-red, somewhat resinous residue remained, which left a bright yellow crystalline substance on treatment with alcohol; this, after purification by washing with hot alcohol, weighed 1·6 grams. The crystalline substance on boiling with ethylic acetate was separated into two portions, one soluble, α-benzileosazone, the other a canary-yellow insoluble powder identical with v. Pechmann's dibenzaldiphenylhydrotetrazone (*loc. cit.*); on recrystallisation from benzene, the latter formed silky needles melting at 186°. The air-dried substance was analysed.

0·2115 gave 27·4 c.c. moist nitrogen at 15° and 732 mm. N = 14 8.
Calculated for $C_{26}H_{22}N_4$. N = 14·36 per cent.

It is very insoluble in almost all solvents, and dissolves but sparingly in hot benzene and chloroform. With sulphuric acid, it gives a characteristic blue coloration, and on heating with phenylhydrazine it is reduced to the original benzalphenylhydrazone.

Action of Alcoholic Potash on Dibenzaldiphenylhydrotetrazone.

The hydrotetrazone (0·5 gram) was dissolved in benzene, and caustic potash (1·5 grams) in alcoholic solution added; a precipitate formed at first, but on heating it dissolved and a dark brown liquid was obtained. After boiling for half-an-hour, using a reflux condenser, alcohol was added and the crystals which separated were collected and recrystallised from a mixture of benzene and alcohol. They melted at 224—225° and showed all the properties of β-benzileosazone. On analysis, they gave the following numbers.

0·156 gave 0·4560 CO_2 and 0·0805 H_2O. C = 79·72; H = 5·73.
Calculated for $C_{26}H_{22}N_4$. C = 80·00; H = 5·64 per cent.

α-Benzileosazone. That portion of the substance obtained by the action of sodium ethoxide and iodine on benzalphenylhydrazone, which is soluble in ethylic acetate, and which forms the bulk of the product, separates from the concentrated solution in small prismatic yellow crystals melting at 206°. When purified by recrystallisation from a mixture of benzene and alcohol, it forms yellow prismatic needles, melting and decomposing at 208°. On analysis, it gave numbers agreeing with those required for benzileosazone. The substance was dried in a vacuum.

0·1196 gave 15·5 c.c. moist nitrogen at 15·5° and 731 mm. N = 14·56
0·1330 gave 0 3915 CO_2 and 0·0660 H_2O. C = 80·25; H = 5·51.
Calculated for $C_{26}H_{22}N_4$. C=80·00; H = 5·64; N = 14·36 per cent.

It is practically insoluble in alcohol, but dissolves slightly in ether and more easily in acetone, ethylic acetate, chloroform and benzene. A determination of the molecular weight was made in benzene solution by Raoult's method, and gave the following numbers.

Weight of substance taken ... = 0 2425 gram.
Weight of benzene taken ..... = 13 6595 grams.
Depression of freezing point .. = 0 21°.

	Calculated for $C_{26}H_{22}N_4$	Found.
Molecular weight...........	390	414

It undergoes no change when heated with dilute acids, the residue melting as before at 208°, but with concentrated sulphuric acid a wine red coloration is produced identical in shade with that produced from β-benzileosazone; this changes to green on adding a drop of ferric chloride, or potassium dichromate solution. If water be added to the sulphuric acid solution, a strong smell of benzaldehyde is produced, and the colour changes to yellowish-brown.

Transformation of α-Benzileosazone into the β-modification.

1.—*By means of phenylhydrazine.*—0 5 gram of the α-osazone was heated for an hour with excess of phenylhydrazine in a tube provided with a reflux condenser. On cooling the orange-red liquid, and adding acetic acid and water, a substance separated which was practically insoluble in alcohol; it was purified by repeated washing on the filter with this liquid, and by twice recrystallising from a mixture of chloroform and alcohol. It then melted at 224° and showed all the properties of the β-osazone.

2.—*By ethylic succinate.*—1 gram of α-benzileosazone was heated with 4 grams of ethylic succinate (b. p. 217°) to the boiling point of the mixture. The osazone dissolved, and the liquid darkened in colour until it became a deep brown. After five minutes, the action was complete; the flame was then removed, alcohol added, and the precipitate recrystallised from benzene and alcohol. A substance melting at 224—225° was thus obtained, the yield being 50 per cent. on the α-osazone used. On analysis the product gave the following numbers:

0·1550 gave 0·4545 CO_2 and 0·084 H_2O. C = 79 98; H = 6·02.
0·1350 gave 0·3970 CO_2 and 0·0745 H_2O. C = 80 20; H = 6·13.
Calculated for $C_{26}H_{22}N_4$. C = 80·00; H = 5 64.

It has, in addition, all the properties of β-benzileosazone.

3.—β-benzileosazone is similarly produced on heating the α-compound dissolved in ethylic benzoate (b. p. = 211°) or ethylic malonate (b. p. = 195°). Since it is obtained in the latter case, it would appear that the change may be brought about at a temperature below but near to the melting point of the α-osazone.

4.—*By heating with alcohol at* 200°. 1 gram of the α-osazone was heated in a sealed tube with 20 c.c. of absolute alcohol at a temperature from 180° to 205° for two to three hours. The clear orange-coloured liquid contained long needles of the β-osazone and on opening the tube a smell of benzaldehyde was noticed, as well as the presence of alkaline vapour. A partial decomposition of the osazone has, therefore, taken place. The crystals proved to be the β-osazone melting at 225°.

Relative Properties of the two Osazones.

1.—*Solubilities.*—Since there is a very great difference in the solubilities of the stereoisomeric osazones described by Anschütz and Pauly (*loc. cit.*) it was of interest to examine the two osazones with respect to this property. For this purpose, acetone was chosen as the solvent, and the two isomerides were found to give small though definite differences in their solubility in this liquid.

α-Benzileosazone.—1·699 grams of the acetone solution at 18—19° left on evaporation 0·0275 gram of the osazone; hence 100 parts of acetone dissolve 1·65 parts of the α-compound.

β-Benzileosazone.—2·4165 grams of the acetone solution at 18—19° left on evaporation 0·0565 gram of the solid; hence 100 parts of acetone dissolve 2·4 parts of the β-compound.

The solubility of the two substances in ether was likewise shown to differ to a small extent.

2.—*Behaviour towards Oxidising Agents.*—When dissolved in acetic acid and treated with potassium dichromate solution, the α-osazone instantaneously gives a dark red coloration; this quickly disappears, and on the addition of more dichromate the liquid assumes an orange-red colour. The β-osazone does not yield the initial red colour when treated in this way but, after standing, acquires a similar orange-red tint. On carrying out the oxidation in ethereal solution with potassium permanganate and hydrochloric acid (*see* Anschütz and Pauly, *loc. cit.*), a dark red solid was obtained from the α osazone, but it could not be crystallised.

v. Pechmann has proposed amylic nitrate as an ozidising agent for imido-hydrogen groups, and it was hoped by this means to obtain an osotetrazone from the α-osazone. For this purpose, the α-osazone was dissolved in benzene, and treated with excess of this oxidising agent. As each drop of the nitrite touched the liquid, a bright red coloration was produced which immediately disappeared, but on boiling the mixture, the colour returned. After heating for half an hour, a precipitate had formed in the liquid, and this was removed by filtration and crystallised from alcohol. It did not melt below 250°, but since it gave Liebermann's reaction with phenol and sulphuric acid it is probably a nitrosamine; the quantity obtained was too small to admit of further examination. The resinous residue left on evaporating the filtrate was extracted with light petroleum, and this, on evaporation, yielded a dark red resin, which, although it was not obtained in a crystalline form, gave β-benzileosazone on heating with excess of phenylhydrazine, so that it is probably an osotetrazone.

When β-benzileosazone is subjected to similar treatment with amylic nitrite, it does not yield a dark red, but rather an orange-yellow solution, and appears to suffer decomposition. We were unable to obtain either the nitrosamine, or a resin similar to that above-mentioned.

We hope to be able to repeat these oxidation experiments with larger quantities of the substances.

3.—*Behaviour towards Sulphuric Acid.*—(a.) *α-osazone, m. p.* 208°.—1 gram of the finely powdered substance, placed in a small round-bottomed flask, was well shaken with 10 c.c. of concentrated sulphuric acid; after half an hour, 100 c c. of water was run in, when the original wine red colour immediately changed to a dull brick red. The contents of the flask were now distilled in a brisk current of steam, the concentration of the liquid being kept approximately constant; the distillation was continued for five hours and large amounts of benzile (m. p. 93—94°) passed over together with benzaldehyde. On making the contents of the flask alkaline, and again distilling in steam, ammonia, aniline, traces of phenylhydrazine and of an isonitrile were detected.

The experiment was repeated with 2 grams of the α-osazone, but this time the flask was allowed to stand only 10 minutes before the addition of the water, and further, towards the end of the experiment, the concentration was allowed to increase. Under these conditions white shining hexagonal plates were deposited in the condenser; they crystallised from alcohol in nacreous laminæ, melting at 120—121°, and showing all the properties of triphenylosotriazole (Auwers and V. Meyer, *loc. cit.*); the other products before-mentioned were likewise formed.

(b.) *β-osazone, m. p.* 225°.—One gram of the finely powdered substance was treated exactly as the first portion in (a). In this case, the distillate contained no trace of benzaldehyde, but benzile was formed in large quantity. On rendering alkaline and again distilling in steam, ammonia, aniline, and traces of phenylhydrazine were found in the distillate.

If the experiment be varied by allowing the substance to stand only 10 minutes with the concentrated acid, and also gradually concentrating the liquid during the distillation, another product was formed in addition to the above. Towards the end of the operation, a white crystalline substance was deposited in very small quantity in the condenser; this crystallised from alcohol in flat rhombic plates, and melted at 115°. It was soluble in ether, but insoluble in alkalis, acids, and water, and differs both in melting point, crystalline form, and solubility from the triphenylosotriazole obtained with the isomeric substance. The quantity, however, was too small for further examination.

These experiments with the two osazones were several times repeated, and under the above conditions the same characteristic substances were always formed.

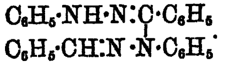
Oxidation of Benzalphenylhydrazone by Amylic Nitrite.—As mentioned in the introduction, v. Pechmann obtained dibenzaldiphenylhydrotetrazone by oxidising benzalphenylhydrazone with amylic nitrite in ethereal or light petroleum solution. On repeating his experiments, we obtained somewhat different results and an account of them will perhaps be of interest. Five grams of benzalphenylhydrazone was dissolved in ether, and about 5 grams of amylic nitrite added to the solution; the mixture, heated on the water bath, gave an orange-yellow solution at first, but on further heating this darkened and deposited yellow crystals. After six hours, these were collected and washed with ether and alcohol; the yield of dibenzaldiphenylhydrotetrazone (m. p. 185—186°) thus obtained was about 0·8 gram.

The filtrate from the crystals was concentrated by evaporation, treated with alcohol and filtered. On the filter there remained about 0·8 gram of a yellow crystalline substance which, after recrystallisation from a mixture of alcohol and benzene, melted at 202°. An analysis gave the following results.

0·154 gave 0·4505 CO_2 and 0·076 H_2O. $C = 79·79$; $H = 5·49$.

It is more soluble in alcohol than the α-osazone, and gives benzaldehyde on boiling with dilute acids, and a blue-green coloration on treatment with concentrated sulphuric acid It does not appear to be changed by heating with alcoholic potash or with ethylic succinate, but phenylhydrazine. on boiling, reduces it to benzalphenylhydrazone. On treatment in acetic acid solution with potassium dichromate, a claret colour which rapidly darkens is produced. This would seem to indicate the presence of oxidisable hydrogen.

The constitution of this substance is not yet absolutely determined, but from this summary of its properties it appears not to be identical either with the α-osazone, or with dibenzaldiphenylhydrotetrazone. Its behaviour corresponds more nearly with the constitution represented by the formula



$$\begin{array}{l} C_6H_5\cdot NH\cdot N:\underset{|}{C}\cdot C_6H_5 \\ C_6H_5\cdot CH:N\cdot N\cdot C_6H_5 \end{array}.$$

We are at present engaged in a further study of the whole subject, and hope to be able to extend the reactions described in this paper to other aldehydrazones.

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LXVIII.—*Preparation of the Active Lactic Acids and the Rotation of their Metallic Salts in Solution.*

By T. PURDIE, Ph.D., B.Sc., and J. WALLACE WALKER, M.A.

IN his recently published work, *Die Lagerung der Atome im Raume*, van't Hoff has emphasised the value of determinations of the molecular rotations of the salts of active acids in solutions of varying concentration. Their importance. as he points out, lies in the fact that only thus can comparable values be obtained for the rotations of the different optically active acids of a series. With the exception, however, of the derivatives of amylsulphuric acid, investigated by Carrara and Gennari (*Gaz. Chim*, 1894, **24**, ii, 484), and glyceric acid by Frankland (Trans., 1893, **63**, 296), the substances examined have been of more or less complex constitution; and few, even of these, are closely allied to each other. As lactic acid, besides being the simplest of its series, is of great interest historically in connection with stereo-chemistry, we have endeavoured to use the method already described for the preparation of the active acids (Trans., 1893, **63**, 1143) to obtain sufficient material for the examination of the salts. We have also determined the depression of the freezing points of aqueous solutions of some of these salts, with the double object of detecting the existence or non-existence of a racemoïd compound in solution, and of determining, in a rough way, the amount of electrolytic dissociation in them.

We had reason to believe that, by the method referred to, both active lactic acids could be procured in quantity with comparative ease. In attempting, however, to carry out the process on a larger scale, unexpected difficulties were encountered, necessitating certain modifications of the method originally used, and they were in fact overcome only after numerous and somewhat tedious experiments. A solution of zinc ammonium lactate prepared as described (*loc. cit.*) did not yield alternate crops of dextro- and lævo-gyrate double salt with the regularity observed in the experiments on a smaller scale but often deposited nothing but inactive zinc lactate, whilst in other cases it was the inactive racemoïd double salt, or mixtures of the two active double salts. The irregularity was evidently due to the change in concentration and composition of the solution produced by the removal of successive crops of crystals, and when a solution had once ceased to yield the active salts, we found it extremely difficult to restore the favourable conditions of concentration by adding one or other of the constituents. The purification of the crude double salt by recrystallisation from ammonia, as formerly described, also proved uncertain in its results when the substance contained any considerable proportion of inactive salt. Lastly, we found that the separation of active zinc lactate in a state of purity from a mixture containing a considerable quantity of racemoïd lactate is attended with much loss of material in spite of the great difference in solubility of the two forms; the tendency exhibited by both of them to form supersaturated solutions causes irregularities in the deposition of the crops of crystals, rendering it difficult to carry out a systematic fractional crystallisation. Thus, from a mixture containing about 75 per cent. of active zinc lactate, the purest fraction obtained, after a number of crystallisations, amounted only to about a fourth of the active salt originally present, and, from polarimetric observations, this still contained several per cent. of racemoïd lactate. In other instances, where the progress of the purification was observed by estimations of the water of crystallisation in successive crops of crystals, we found that, after a certain limit of purity was reached, the racemoïd salt was eliminated very slowly by repeated crystallisation.

Certain modifications of the method of procedure were therefore adopted with respect to (1) the production of the active zinc ammonium salts, (2) their recrystallisation, and (3) the final purification of these salts.

Production of the Active Zinc Ammonium Lactates.—The researches of Wyrouboff, van't Hoff, and others have clearly established the general principle of procedure for the spontaneous resolution of a racemoïd compound by crystallisation, that the crystallisation, namely, must be effected above or below a certain temperature, the "transition point," according as the mixture of the two active forms is the stable form of equilibrium at high or low temperatures. Our experiments, so far as they go, indicate that the racemoïd compound represents the stable system at lower temperatures in the case of zinc ammonium lactate. The active zinc ammonium lactates crystallise with $2H_2O$, the racemoïd salt with $3H_2O$. If the latter is the stable form at lower temperatures, a mixture of equal parts of the active salts ought to be converted into the racemoïd salt on adding the calculated quantity of cold water. The results of the following experiment indicate that this is probably the case. When 2 grams each of active zinc ammonium lactate, of the racemoïd salt, and of an intimate mixture of the two oppositely active salts were exposed for some days in a damp atmosphere, the mixture of active salts increased 0·04 gram in weight, while the weight of the other two salts remained almost unchanged, the conditions being identical; when the three specimens were placed under a bell-jar over moistened filter-paper, the mixture underwent a further increase of 0·351 gram, the racemoïd salt gained 0·249 gram, the active salt 0·012 gram, and when they were once more exposed to ordinary air, the racemoïd and active salts lost the water which they had absorbed, whilst the mixture of active salts on the other hand, though it became nearly constant in weight after some weeks, still retained 0·062 gram of the absorbed water. One molecular proportion of water would amount to 0·088 gram. The results of the experiment are not absolutely conclusive, as the double salts are readily decomposed into their constituent salts by water, and the gain in weight may have been due to the formation of hydrated inactive zinc lactate; in this case, however, some visible quantity of the uncrystallisable ammonium lactate should have been left. Experiments on the relative quantities of racemoïd and of active double salts obtainable from a cold solution of zinc lactate in ammonium lactate also indicate that the former is the stable system of equilibrium at the ordinary temperature. A supersaturated solution was prepared as described in a previous paper (*loc. cit.*) and divided into two equal parts, which were sown respectively with nucleï of mixed active and of racemoïd salt; the crystalline deposits when air dried weighed respectively 3·5 grams and 24 grams. A solution from which the two active forms have been deposited and separated by filtration is converted quickly into a thick, crystalline mass of racemoïd salt when a nucleus of the latter is stirred into it.

Though the mixture of active zinc ammonium salts probably represents the stable system of equilibrium at higher temperatures, there is a practical difficulty in obtaining the salts from a hot solution, for they do not crystallise from such a solution if it contains a large excess of ammonium lactate, and, unless there is such an excess, they are resolved into ammonium and zinc lactates. We have therefore had to crystallise the salts from cold supersaturated solutions prepared in the manner already described (*loc. cit.*). The following proportions, however, were found more advantageous than those previously used:—Lactic acid syrup ($d = 1·21$) 1000 c.c., zinc lactate 560 grams, volume of solution 2000 c.c. As a solution of this degree of dilution is very prone to deposit inactive zinc lactate, every precaution must be taken to avoid the introduction of nucleï of this salt; the solution should therefore be boiled till the last traces of zinc lactate are dissolved, and poured while hot into a clean vessel. The solution having been rapidly cooled, and some of the finely powdered, pure active zinc ammonium lactate added, it is thoroughly stirred without rubbing the sides of the vessel, which is apt to induce the crystallisation of inactive zinc lactate, or of the racemoïd double salt. A solution such as that mentioned should yield in 12 to 24 hours about 100 grams of active salt. The deposit is separated from the mother liquor with the aid of a filter pump, and is washed with alcohol; the mother liquor is again boiled, 100 grams of zinc lactate having been added to it, and enough water to make up the solution to its original volume, and the crystallisation of the oppositely active salt is then induced by thoroughly stirring in some of the proper nucleus.

The successful alternate crystallisation of dextrogyrate and lævogyrate salt depends on maintaining the solution in a suitable state of concentration. If the constituents are present in proper proportion, the nuclei which are added form threads of microscopic crystals as they slowly sink in the syrup, and the solution becomes turbid in the course of two or three hours. In the course of 12 to 24 hours the crystalline crop should have subsided as a thick, heavy sludge, from which most of the syrup can be poured off. The production of inactive zinc lactate instead of the active double salt, which is readily detected with the aid of the microscope, is an indication of an excess of water; the solution in this case must be again boiled and concentrated slightly by evaporation. Should the solution on the other hand fail to crystallise in 12 to 24 hours, which indicates an insufficiency of water, no purpose is served by leaving it longer, as after that time the crystallisation of the racemoïd double salt sets in; in this case therefore the solution must be again boiled after a little water has been added. Failure to crystallise after dilution indicates an insufficiency of zinc lactate. Even when the crystallisation of the active double salt is proceeding satisfactorily, no advantage is gained by leaving the process to go on longer than the time indicated, for although a larger deposit will be obtained, the substance will usually be much less optically active, sometimes indeed almost inactive, the inactivity being due in this instance to the deposition of the two active forms. We have had frequent occasion to notice that, though the first deposit of salt is invariably active in the same sense as the nucleus used, this crystallisation is followed by that of the oppositely active isomeride. A line of demarcation can in fact sometimes be seen in the deposit separating the two layers of the oppositely active salts.

As an example of a successful series of crystallisations, we may give that of a solution of the size and strength already quoted, which yielded in 12 crystallisations 610 grams of dextro- and 612 grams of lævogyrate salt, containing, on an average, as determined by the polarimeter, about 90 per cent. of active substance, and, not unfrequently, equally active crops of over 200 grams were obtained at a single crystallisation. After some practice in carrying out the process, these optically active salts can, in fact, be procured with great ease in any quantity that may be desired.

Recrystallisation of the Active Zinc Ammonium Lactates.

Though the crude active zinc ammonium lactate is frequently produced in a state approaching purity, many of the crops contain much racemoid salt, which must be, for the most part, eliminated before the double salt is converted into zinc lactate. Of various methods of purification, we find that the following gave the best results:—If the salt is feebly active, an 8 per cent. solution, giving a rotation, say, of 20 minutes in a 200 mm. tube, it is shaken for a few minutes with so much cold water as would be required to form an 8 per cent. solution of the active salt present, and the inactive zinc lactate which is thus produced is quickly separated by filtration. The filtrate, as it contains an excess of active ammonium lactate, readily yields the active crystalline double salt, when a nucleus is added to the residual syrup obtained by evaporation; 30 to 50 per cent. of the active salt originally present may be thus recovered, the activity of which will have increased to over 50 minutes. If the crude double salt shows an activity of about 50 minutes under the conditions mentioned above, it may be crystallised as formerly described from dilute ammonia; if the solution, after being sufficiently evaporated, is cooled with ice and stirred with a nucleus of the proper kind, the salt separates at once as a crystalline sludge, which will be found to be an approximately pure salt (rotation about 55 minutes at 10°); the mother liquor is used for crystallising successive similar crops of crude double salt until, owing to the inactive substance having accumulated in the solution, the activity of the recrystallised salt begins to fall. In the case of zinc ammonium salt of intermediate activity, giving a rotation of from 30 minutes to 50 minutes under the conditions mentioned, we find that crystallisation from ammonia does not give very satisfactory results owing to the deposition of a basic inactive zinc ammonium lactate; neither in this case can the method already mentioned as applicable to more feebly active crops be conveniently employed, as, on treatment with water, active zinc lactate may separate with the inactive zinc salt; crystallisation from ammonium lactate solution, on the other hand, yields excellent results. The requisite solution is obtained by decomposing some of the salt with solution of ammonium carbonate and evaporating the filtered solution until it is no longer alkaline. This mother liquor is used for recrystallising successive crops of crude double salt; the crystallisation is best effected rapidly from the supersaturated solution as already described in the case of crystallisation from ammonia, the salt in this case also being obtained nearly pure.

The zinc ammonium salts prepared by the above methods are sufficiently pure to dissolve readily in three or four times their weight of cold water without leaving any residue of undissolved inactive zinc lactate, and their analyses give results which accord with the formula already assigned to the substance, $C_9H_{15}O_9Zn(NH_4),2H_2O$. Thus the estimations of water by loss of weight in a vacuum, and of zinc and ammonium in a specimen of the salt which gave the polarimetric reading, +56 minutes, under the conditions mentioned above, were respectively 9·34, 16·96, and 4·88 per cent., the corresponding calculated numbers being 9·32, 16·93, and 4·66 per cent.

It has been previously shown that the specific rotation of solutions of the zinc ammonium lactates rises with dilution. The specific rotations of different specimens at the same concentration, quoted in previous papers, were, however, not very concordant, and we encountered similar variations in the course of the present investigation. We now find that these discrepancies were due to the fact that the specific rotation of the salt increases very considerably with rise of temperature. As no account was taken of temperature in our former observations, we quote the following determinations of specific rotation, made on a specimen prepared from pure zinc lactate: $c = 8·002$, $l = 400$ mm., α at 2° $= -1·74°$, α at 14° $= -1·87°$, hence $[\alpha]_D$ at 2° $= -5·44°$, $[\alpha]_D$ at 14° $= -5·84°$. The specific rotations 6·06° and 6·44°, quoted in previous papers, were taken at summer temperatures; we have reason, however, to believe that the second of these two observations is too high.

Production of Pure Active Zinc Lactates.

Inasmuch as the active zinc ammonium lactates crystallise together as a mixture from ammonium lactate solution, and may possibly crystallise similarly even from ammonia solution, we have found it necessary, in spite of the correspondence of the results of their analysis with the calculated composition, to convert them into the well characterised zinc salts in order to be assured of the complete purity of our material. The contamination of active salt with even a small quantity of a mixture of the oppositely active forms can in this manner be readily detected; for, as we have previously shown, a mixture of the active zinc lactates, when crystallised from aqueous solution, yields racemoid lactate, and the former, as is well known, crystallise invariably with $2H_2O$, the latter with $3H_2O$, corresponding respectively to 12·88 and 18·16 per cent. of water. The water of crystallisation of the zinc salts is the test of purity on which we have invariably relied; the lactates being feebly active, polarimetric observations alone would not suffice to detect the presence of such an admixture of racemoïd salt as might produce serious error, in the event of the material being afterwards used for the production of more active substances.

In a previous communication (Trans., 1893, **63**, 1153), it has been shown by one of us that the purest specimens of the active zinc ammonium lactates obtainable by recrystallisation, yielded active zinc lactates so free from racemoid salt that the pure active salts could be readily obtained from them by recrystallisation. The salts contained the calculated water of crystallisation, and their activity agreed with that of zinc sarcolactate as determined by Wislicenus (*Annalen*, 1873, **167**, 332). On carrying out these experiments on a larger scale, we failed to obtain the salts with such a high degree of activity as formerly; we found invariably the specific rotation 6·3° for both isomerides instead of 6·8°, for the concentration 7·48, and the water of crystallisation was always several tenths per cent. too high. We were therefore led to a prolonged investigation of different methods of obtaining the active zinc lactates from the zinc ammonium double salts with the view of eliminating from them the inactive racemoid salt with which we supposed them to be contaminated. After analysing numerous preparations, we found that the excess in water of crystallisation was due, in most cases, to traces of ammonia and hygroscopic water, and that, with proper precautions, the active salts can be readily obtained so free of racemoïd salt as to yield results on analysis differing by only one-tenth from the calculated percentage of water of crystallisation. The specific rotations, however, of the salts, the purity of which was proved by analysis, and by the fact that the numerous specimens of both dextrogyrate and lævogyrate forms prepared by different methods possessed identical activity, were still found to be lower than the values usually assigned to them, and previously found by ourselves. As the specimens of active zinc lactate referred to had usually been obtained from a hot aqueous solution by evaporation, it seemed possible that the low activity might be due to the presence of some mixed oppositely active salts produced by the resolution of inactive zinc lactate into its components when crystallised under the conditions mentioned. This supposition, however, was negatived by the results of experiments in which inactive zinc lactate was crystallised under precisely similar conditions in the presence of nuclei, first of dextrogyrate, and then of lævogyrate salt; pure inactive zinc lactate was in each case deposited, containing 18·15 and 18·17 per cent. of water, the calculated percentage being 18·16.

It was also found that the activity was not altered by partial precipitation of the aqueous solution of our specimens of active zinc lactate by the addition of alcohol, which it was supposed would remove the inactive salt present. A quantity of zinc lactate having 12·89 per cent. of water of crystallisation and a specific rotation −6·32° ($c = 7·48$), was dissolved in water, and one-third of the salt was then separated by the addition of alcohol. The salt obtained from the filtrate contained 12·89 per cent. H_2O, and showed the specific rotation −6·28°, and the precipitated salt when recrystallised from water contained 12·90 per cent. H_2O, and showed the specific rotation −6·35°. We discovered at length that the discrepancy was due to the fact, which, so far as we know, has not yet been noticed, that the specific rotation of zinc lactate varies to a marked degree with temperature. Our former observations, and no doubt also those of Wislicenus—though no temperature is quoted by him—were taken in summer time, whilst those which gave the low results were all taken during winter at about 10°. The instrument at our disposal not being furnished with a water-jacket did not admit of our taking accurate observations at varying temperatures, but we satisfied ourselves that the specific rotation of the salt increases with rise of temperature, and that the variation is considerable within the ordinary range of the temperature of the atmosphere. To assure ourselves of the purity of our preparations we prepared zinc sarcolactate from extract of meat by Wislicenus' method, and found that under the same conditions of temperature it had the same specific rotation as the purest zinc lactate procured by our method, namely, −6·29°, at the concentration 7·48. As already stated, however, the water of crystallisation is the test of purity to which we have attached most importance. In the following description of the preparation of the pure zinc lactates, the specific rotations which are quoted refer to the concentration just mentioned at about 10° C. In all exact observations of specific rotation, a 400-mm. tube was used, and in estimating water of crystallisation, in order to insure its maximum value being found, the salt was heated till quite constant at 115—120°, instead of at 105° as has been previously done, about 2 grams of air-dried salt being used for each estimation. The following were the methods chiefly used for obtaining the active zinc lactates from the active double salts, with examples of the results obtained:—

First Method.—Crude double salt ($\alpha = 45'$, when $c = 8$ and $l = 2$)

was treated with so much cold water that active zinc lactate was retained in solution and inactive zinc lactate precipitated; the filtered solution being sufficiently evaporated yielded active zinc lactate which, on recrystallisation from a hot solution, was obtained in large, glassy crystals. Results of analysis: found, $H_2O = 13{\cdot}04$, $Zn = 23{\cdot}38$ per cent.; calculated, 12·88 and 23·41 per cent.; specific rotation, +6·45°; the specific rotation of lævogyrate salt similarly obtained was −6·35°. The mother liquors containing much active ammonium lactate can be used for recrystallising crude double salt. This method was afterwards abandoned as it was found that the active zinc lactate was apt to be contaminated with active zinc ammonium lactate. The following process gave excellent results when fairly pure zinc ammonium salt was employed.

Second Method.—The finely powdered, recrystallized double salt is shaken with about 2½ times its weight of cold water; if approximately pure, it dissolves readily, leaving very little residue; but, in the course of a few minutes, owing to the decomposing action of the water on the double salt, an abundant deposition of active zinc lactate is produced. The solution is filtered rapidly before the precipitation occurs, and is allowed to stand some hours. The deposited salt is then separated by filtration, slightly washed, and recrystallised from water until the water of crystallisation is within one-tenth per cent. of the calculated quantity. The salt may be crystallised either by evaporating the hot solution, keeping the hard glassy crystals of the salt which separate always under the surface of the water, or by allowing the hot solution to cool, in which case it is obtained as a fine crystalline powder. Two crystallisations are usually necessary before a satisfactory result for the water of crystallisation is obtained. The following examples may be quoted: 308 grams of lævogyrate zinc ammonium salt, after two crystallisations, yielded 135 grams of zinc salt; $H_2O = 12{\cdot}98$ per cent. $[\alpha]_D = -6{\cdot}28°$, the water found after the first crystallisation being 13·29 per cent.; 343 grams of dextrogyrate zinc ammonium salt gave similarly 160 grams of dextrogyrate zinc lactate, the loss of weight of which at 130° was 13·07 per cent.; this number, however, was reduced after another crystallisation to 12·93 per cent. $[\alpha]_D = +6{\cdot}3°$.

In order to recover the active substance from the mother liquors from which the zinc salts have been precipitated, they are boiled with sufficient lime to remove the ammonia and zinc contained in them; the lactic acid, which is obtained from the filtered solution of the calcium salt by adding to it the calculated quantity of sulphuric acid, filtering and extracting the concentrated filtrate with ether, is converted into zinc salt, which is then kept in agitation for some hours with a quantity of cold water insufficient for complete solution. The filtered liquid on evaporation yields practically pure active zinc lactate; the salt obtained in this manner from the mother liquor of the first of the two experiments quoted above gave 12·99 per cent. for water of crystallisation, and the specific rotation —6·2°, and that from the second experiment 13·07 per cent.—after recrystallisation 12·97 per cent. of water.

By the methods described we have prepared several kilograms of the two active zinc lactates, the specific rotations of the different preparations agreeing closely with those quoted, and the water of crystallisation varying from 12·86 to 12·98 per cent. A large proportion of the less pure salt remains in the mother liquors, but it can be readily recovered from these in a purer state as active zinc ammonium lactate.

With regard to the amount of racemoïd salt that may be contained in the active zinc lactate, an excess of one-tenth per cent. in the water of crystallisation corresponds to 1·9 per cent. of the former, but it may be pointed out that the estimations of water of crystallisation in many specimens did not differ by more than 0·05 per cent. from the calculated number, and, moreover, as the salts were in every case only air dried, part or probably even the whole of the excess in question may be due to hygroscopic water.

Metallic Salts of the Active Lactic Acids.

Owing to the difficulty of obtaining lactic acid free from anhydride, we have confined our observations on optical activity to its salts. The only compounds of this class which have been hitherto prepared are the sarcolactates of calcium, zinc, and silver, and of these only the two former have been examined optically; in addition to these compounds, we have investigated the salts of lithium, sodium, potassium, strontium, barium, magnesium, and cadmium, and also the zinc ammonium salt. We have, however, as a general rule, prepared only one of the two oppositely active forms in each case. The active acids used in the preparation of these salts were procured from the pure active zinc lactates by precipitating the zinc with lime, decomposing the solution of the calcium salt thus obtained by the addition of the calculated quantity of sulphuric acid, and extracting with ether the syrup left after filtration and subsequent evaporation. The crystallisable salts were in general prepared by warming the aqueous solution of the acid with excess of the carbonate of the metal until neutral, and evaporating until the salt crystallised out on standing. We append our observations on the character and composition of those salts which were obtained in the crystalline state.

Lithium l-*lactate.*—The salt crystallised from a thin syrup in pearly scales. Estimations of lithium as sulphate, made on the salt which had been dried at 100°, gave 7·26 and 7 30 per cent., the calculated percentage for the anhydrous salt being 7·29. The salt is not deliquescent, nevertheless, after being dried by exposure to the air during many weeks, it lost 9·21 per cent. of water on being dried at 100°; the calculated percentage for $\frac{1}{2}H_2O$ is 8 57.

Calcium d-*lactate.*—This salt, which was procured from the solution resulting from the decomposition of the pure zinc salt with lime, after the excess of the latter had been removed with carbonic anhydride, was found by a calcium estimation to have the composition assigned to it by Wislicenus; found, 13·40 per cent.; calculated for,

$$C_6H_{10}O_6Ca,4\frac{1}{2}H_2O,$$

13·38 per cent.

Strontium l-*lactate.*—The salt crystallised from a thick aqueous syrup in opaque, white masses of microscopic prisms, and from a more dilute aqueous solution to which alcohol had been added in larger isolated, transparent prisms. Estimations of strontium as sulphate, and of water in the salt which had been dried at 100°, gave the following results: found, Sr 30·78 and 30·74 per cent.; H_2O lost at 125°, 6·34 per cent. Calculated for $C_6H_{10}O_6Sr,H_2O$; Sr, 30·86 per cent.; H_2O, 6·35 per cent. A sample of the salt which had been long dried in air, when heated at 100°, lost 16 92 and 16·95 per cent.; the calculated percentage for $3H_2O$ on the salt $C_6H_{10}O_6Sr,4H_2O$ is 16·00. Attempts to remove the hygroscopic water indicated by the latter numbers were unsuccessful, as the compound loses water of crystallisation when placed over sulphuric acid. The air-dried salt therefore contains, no doubt, 4 mols. H_2O; 1 mol. is retained at 100°, and the salt becomes anhydrous at 125°.

Magnesium d-*lactate.*—This salt was obtained from a concentrated aqueous solution as a crystalline powder. Results of analysis: heated at 140°, the air-dried salt lost 23·78 per cent. of water, and contained 9·44 per cent. of magnesium estimated as oxide; the corresponding numbers calculated for $C_6H_{10}O_6Mg,3\frac{1}{2}H_2O$ are 23·74 and 9·19. The salt, after being dried over sulphuric acid, lost 14·93 per cent. of water at 125°, and contained 10·57 per cent. of magnesium, estimated as oxide; the calculated numbers for $C_6H_{10}O_6Mg,2H_2O$ are 15·10 and 10·23. The air dried salt therefore contains $3\frac{1}{2}H_2O$, of which $1\frac{1}{2}$ mols. are given off over sulphuric acid, and the remaining 2 at 125°.

Cadmium d-*lactate.*—This salt crystallised from its aqueous solution in well formed transparent prisms. No satisfactory determination of the water of crystallisation was obtained, as some water was still retained at 190°, and at a somewhat higher temperature the salt decomposed. Estimations of cadmium gave the following results: by precipitation as carbonate and conversion into oxide, 34·90 per cent.;

and as sulphate, 35·18 per cent.; calculated for $C_6H_{10}O_6Cd,1\frac{1}{2}H_2O$, 35 33 per cent.

Silver d-*lactate.*—The salt crystallised well from aqueous solutions, without undergoing decomposition, in long, transparent prisms, which were anhydrous after standing over sulphuric acid. An estimation of silver in the dried salt gave 54·83 per cent. instead of the calculated number 54·82. On adding alcohol to the aqueous solution of the salt, it is converted into a jelly, which becomes a mass of crystals on standing. The alcoholic-aqueous solutions blacken quickly on being heated.

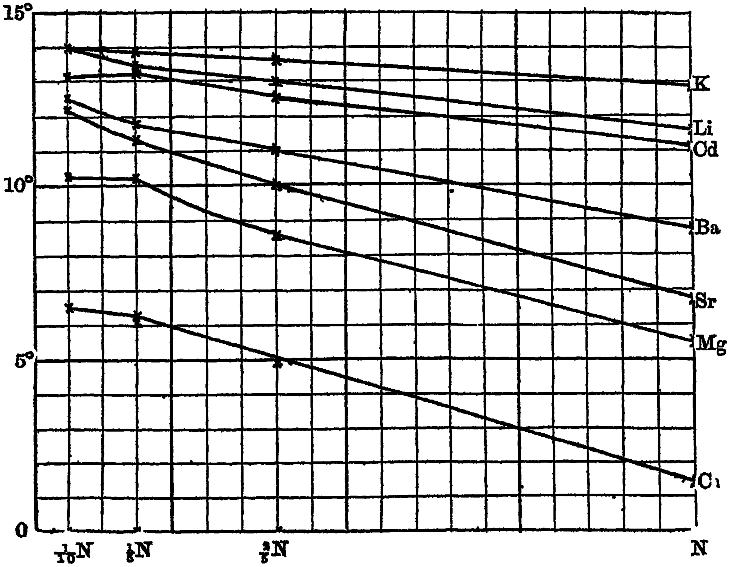
For most of our observations on optical activity and depression of the freezing point, solutions of equivalent concentration of anhydrous salt were employed; normal solutions were in each case first prepared, and from these, by suitable dilution of measured volumes, solutions of the concentrations $\frac{2}{3}$, $\frac{1}{5}$, and $\frac{1}{10}$ normal, were procured. In the case of the salts which have been described, including the zinc and zinc ammonium salts, the normal aqueous solutions were prepared by dissolving the calculated weights of the substances in water, and making up the solutions to 100 c.c., or other required volume; as the salts could not be rendered anhydrous without risk of impairing their activity, the necessary correction was of course made for water of crystallisation. In the case of the aqueous solutions of the sodium and potassium salts, measured volumes of standard solutions of the hydroxides were neutralised with dextrolactic and lævolactic acid respectively, and then diluted with water to the necessary volume; the solutions were heated before being completely neutralised, so as to insure the complete decomposition of any anhydro-acid that might be present. The solution of barium lactate was obtained by neutralising *d*-lactic acid with barium carbonate, finally using barium hydrate, and its concentration was adjusted after an estimation of the barium in an aliquot part. The alcoholic solution of sodium *l*-lactate was prepared by neutralising *l*-lactic acid syrup with an alcoholic solution of sodium ethoxide. To obtain the solution as free from water as possible, the method employed by Wislicenus for obtaining anhydrous inactive sodium lactate was adopted (*Annalen*, 1863, **125**, 50); ether was added to the alcoholic solution, and the viscous mass of sodium salt which was precipitated, was heated at 100° in a vacuum. The residue did not solidify on standing; it was, therefore, dissolved in absolute alcohol, and the concentration of the solution determined by incinerating the residue left on evaporating an aliquot part of it. The residue referred to, when dried at 150°, contained 20·21 per cent. of sodium, the calculated percentage for sodium lactate being 20·54. The alcoholic solution was finally made up to the volume required for normal concentration; and, from this solution, others were obtained by suitable dilution. Some observations on more concentrated alcoholic solutions are quoted; the concentrations of these were separately determined. Alcoholic solutions of potassium *d*-lactate were similarly prepared. The aqueous-alcoholic solutions, with which some observations were taken, were obtained by diluting measured portions of the aqueous and alcoholic solutions with absolute alcohol and water respectively.

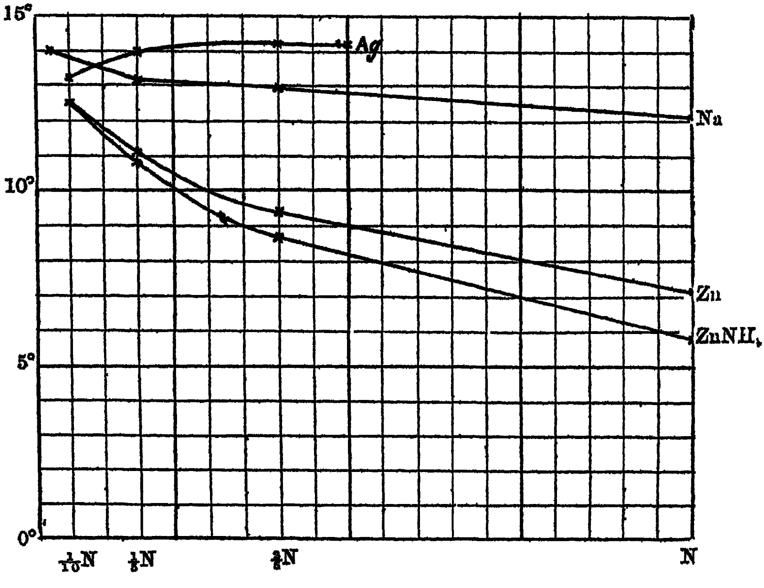
With regard to the degree of accuracy to be attached to our polarimetric observations, it may be stated that the instrument used admitted of readings to only 1 minute, and that except in the case of a few of the more concentrated solutions, a 400 mm. tube was employed. The temperature of observation was about 10°; it varied within a few degrees, but by special experiments on a number of the solutions, we found that the variation in question affected our results to only a very slight extent, except, in the case of concentrated alcoholic solutions which are specially mentioned.

Table I (p. 630) contains our polarimetric observations on aqueous solutions. The salts examined are indicated in the first column by the symbols of their metals, and to each salt is attached its equivalent M. Under α are given the observed angles of rotation for normal, $\frac{2}{5}$, $\frac{1}{5}$, and $\frac{1}{10}$ normal solutions, and under $[\alpha]_D \frac{M}{100}$, the corresponding molecular solutions.

The salts, as already indicated, were prepared in some cases from the dextro-acid, and in others from the lævo-acid, but as the rotation of all the salts examined, in aqueous solution, and within the limits of concentration employed, is in the opposite sense to that of their acid, we have omitted the sign of their activity. Tables II and III contain respectively observations on alcoholic solutions of the sodium and potassium salts, and on aqueous-alcoholic solutions of these and other salts; as the sign of the rotation changes in a number of cases with concentration, we have indicated in these tables by the name of the salt the acid from which each was derived, and have appended to the angles of observation their respective signs. Table IV contains observations on the depression of the freezing point of some of the same solutions which were examined optically. Under Δ are given the observed depressions; the weight of salt P added to 100 grams of water was calculated from the known concentration and observed density *d* 13°/4°. Under $\Delta/P.M$ are given the molecular depressions, and under α the percentage of dissociation calculated from the usual formula $\frac{100 (\Delta - \Delta_0)}{(n - 1) \Delta_0}$, 18 9 being taken as the molecular depression of water.

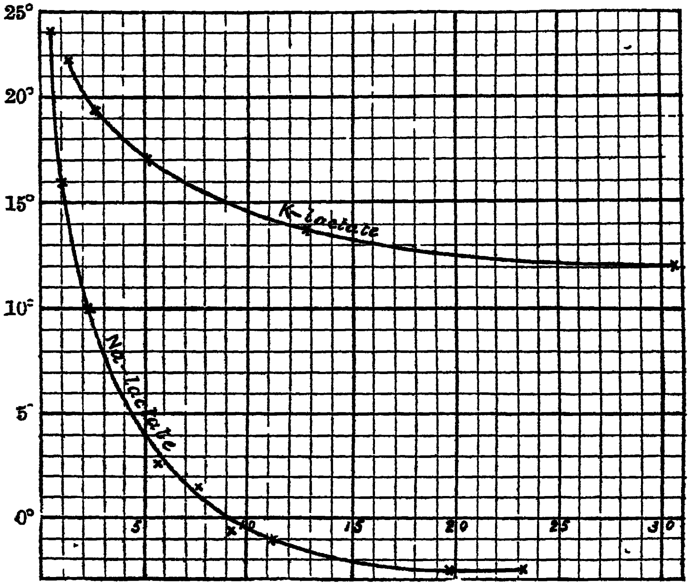
Molecular Rotations of the Lactates in Aqueous Solutions.





In the tables of curves, the molecular rotations are plotted as normals; in the aqueous solutions, the abscissæ represent the concentrations in fractions of a normal solution, and in the alcoholic solutions they represent the concentrations in grams per 100 c.c. To avoid crowding, we have plotted the curves of silver, sodium, zinc, and zinc ammonium separately from the others.

Molecular Rotations of Sodium and Potassium Lactates in Ethylic Alcohol.



Note.—These salts were made from oppositely active acids, but for the sake of comparison we have plotted them as if prepared from the same isomeride.

Table I.—*Aqueous Solutions.*

	M.	a.				$[a]_D \frac{M}{100}$.			
		1.	½.	⅕.	$\frac{1}{10}$.	1.	½.	⅕.	$\frac{1}{10}$.
Li......	96·0	4·66°	2·07°	1·08°	0·56°	11·65°	12·94°	13·50°	11·00°
Na.....	112·0	4·88	2·07	1·06	0·42 *	12·20	12·94	13·25	14·00 *
K......	128·1	5·16	2·18	1·10	0·56	12·90	13·63	13·75	14·00
Ag.....	197·0	2·88 †	2·30	1·12	0·53	14·40 †	14·38	14·00	13·25
Ca.....	109·0	0·51	0·78	0·50	0·26	1·28	4·88	6·25	6·50
Sr......	132·75	2·70	1·59	0·90	0·49	6·75	9·94	11·25	12·25
Ba.....	157·5	3·44	1·75	0·94	0·50	8·60	10·94	11·75	12·50
Mg.....	101·0	2·22	1·38	0·82	0·41	5·56	8·63	10·25	10·25
Zn.....	121·5	2·93	1·51	0·89	0·50	7·33	9·44	11·13	12·50
Cd.....	145·0	4·48	2·02	1·07	0·53	11·20	12·63	13·38	13·25
$ZnNH_4$.	116·67	2·29	1·39	0·87	0·50	5·73	8·69	10·88	12·50

* C — 0·075 normal. † C = ½ normal.

TABLE II.—*Alcoholic Solutions.*

Sodium *l*-lactate.			Potassium *d*-lactate.		
c.	*a.*	$[\alpha]_D \frac{M}{100}$.	*c.*	*a.*	$[\alpha]_D \frac{M}{100}$.
23·208	−2·12°	−2·55°	30·700	−11·48°	−11·98°
19·790	−1·76	−2·49	—	—	—
11·200 (N)	−0·36	−0·90	12·810 (N)	−5·52	−13·80
9·294	−0·18	−0·54	—	—	—
7·467 ($\frac{2}{3}$ N)	+0·40	+1·50	—	—	—
5·600 ($\frac{1}{2}$ N)	+0·56	+2·80	5·124 ($\frac{2}{5}$ N)	−2·72	−17·00
2·240 ($\frac{1}{5}$ N)	+0·80	+10·00	2·562 ($\frac{1}{5}$ N)	−1·56	−19·50
1·120 ($\frac{1}{10}$ N)	+0·64	+16·00	1·281 ($\frac{1}{10}$ N)	−0·87	−21·75
0·560 ($\frac{1}{20}$ N)	+0·46	+23·00	—	—	—

TABLE III.—*Aqueous Ethyl alcoholic Solutions.*

Sodium lactate.

c.	*a.*	$[\alpha]_D \frac{M}{100}$.	
7·467 = $\frac{2}{3}$N	+3·00°	+11·25°	} *l*-lactate
5·600 = $\frac{1}{2}$N	+2·66	+13·30	
2·532	−1·40	−15·47°	} *d*-lactate
1·120 = $\frac{1}{10}$N	−0·69	−17·25	

Lithium *l*-lactate.

c.	*a.*	$[\alpha]_D \frac{M}{100}$.
3·840 = $\frac{2}{5}$N	+2·10°	+13·12°
1·920 = $\frac{1}{5}$N	+1·23	+15·38
0·960 = $\frac{1}{10}$N	+0·69	+17·25

Zinc *l*-lactate.

c.	*a.*	$[\alpha]_D \frac{M}{100}$.
4·86 = $\frac{2}{5}$N	−0·08°	−0·50°

Cadmium *d*-lactate.

c.	*a.*	$[\alpha]_D \frac{M}{100}$.
7·25 = $\frac{1}{2}$N	−1·22°	−6·10°
2·32 = $\frac{4}{25}$N	−0·49	−7·66

Potassium *l*-lactate.

c.	*a.*	$[\alpha]_D \frac{M}{100}$.
21·9987	+7·87°	+11·45°
13·1990	+5·16	+12·52
5·1240 = $\frac{2}{5}$N	+2·47	+15·44
2·5620 = $\frac{1}{5}$N	+1·47	+18·38
1·2810 = $\frac{1}{10}$N	+0·86	+21·50
0·6405 = $\frac{1}{20}$N	+0·45	+22·50

Calcium *d*-lactate.

c.	*a.*	$[\alpha]_D \frac{M}{100}$.
4·360 = $\frac{2}{5}$N	+1·48°	+9·25°

Magnesium *d*-lactate.

c.	*a.*	$[\alpha]_D \frac{M}{100}$.
4·048 = $\frac{2}{5}$N	+0·51°	+3·19°

Strontium *l*-lactate.

c.	*a.*	$[\alpha]_D \frac{M}{100}$.
5·310 = $\frac{2}{5}$N	−0·77°	−4·81°
4·425 = $\frac{1}{3}$N	−0·85	−6·38

TABLE IV.—*Freezing Points.*

Lithium l-*lactate.*

	Δ	*d* 13°/4°.	P.	$\frac{\Delta}{P}M$	*α.*
N........	3·929°	1·0382	10·1890	37·00	95·8
$\frac{2}{5}$N........	1·427	1·0150	3·9320	34·85	84·4
$\frac{1}{5}$N........	0·712	1·0071	1·9435	35·16	85·9
$\frac{1}{10}$N......	0·354	1·0032	0·9662	35·17	86·3

Calcium d-*lactate.*

	Δ	*d* 13°/4°.	P.	$\frac{\Delta}{P}M$	*α.*
$\frac{1}{5}$N.......	0·385°	1·0108	2·2042	38·08	50·8
$\frac{1}{10}$N......	0·210	1·0051	1·0963	41·77	60·5

Strontium l-*lactate.*

	Δ	*d* 13°/4°.	P.	$\frac{\Delta}{P}M$	*α.*
N........	1·866°	1·0783	14·0390	35·28	43·4
$\frac{2}{5}$N.......	0·813	1·0323	5·4228	39·80	53·3
$\frac{1}{5}$N.......	0·431	1·0160	2·6833	42·64	62·8
$\frac{1}{10}$N......	0·218	1·0077	1·3349	43·36	64·7

Barium d-*lactate.*

	Δ	*d* 13°/4°.	P.	$\frac{\Delta}{P}M$	*α.*
N........	2·187°	1·1017	16·6808	41·30	59·4
$\frac{2}{5}$N.......	0·925	1·0416	6·4378	45·27	69·8
$\frac{1}{5}$N.......	0·487	1·0205	3·1850	48·16	77·5
$\frac{1}{10}$N......	0·246	1·0100	1·5841	48·92	79·5

Magnesium d-*lactate.*

	Δ	*d* 13°/4°.	P.	$\frac{\Delta}{P}M$	*α.*
N........	1·805°	1·0458	10·6901	34·10	40·2
$\frac{1}{5}$N.......	0·395	1·0095	2·0418	39·09	53·4
$\frac{1}{10}$N......	0·210	1·0044	1·0158	41·75	60·5

Zinc l-*lactate.*

	Δ	*d* 13°/4°.	P.	$\frac{\Delta}{P}M$	*α.*
$\frac{2}{5}$N.......	0·525°	1·0257	4·9739	25·66	17·8
$\frac{1}{5}$N.......	0·294	1·0126	2·4587	29·06	25·0
$\frac{1}{10}$N......	0·161	1·0059	1·2226	32·00	34·7

Owing to insufficiency of material we were unable to prepare the aqueous alcoholic solutions of Table III by systematic dilution; the following notes will show approximately the proportion of water and alcohol present in each of them. *Sodium lactate.* For the first two, 10 c c. of N alcoholic solution were diluted with water to 15 and 20 c.c. respectively; for the third, 10 c.c. of an aqueous solution were diluted to 25 c.c. with alcohol; for the fourth, 10 c.c. of N aqueous solution were diluted to 100 c.c. with alcohol. *Potassium lactate.* For the first two solutions, 10 c.c. of an aqueous solution ($c = 32·998$) were diluted to 15 and 25 c.c. respectively with alcohol. The remaining solutions of the potassium salt and all the others, excepting the cadmium salt solutions, were prepared by diluting 10 c.c. of the N aqueous solutions with alcohol. *Cadmium lactate.* The solutions were obtained by diluting the N and $\frac{2}{5}$ N aqueous solutions respectively with alcohol.

Aqueous Solutions.—A glance at this table shows that all the salts of the univalent metals which in dilute solution may fairly be assumed to be about 80 per cent. dissociated, namely, lithium, sodium, potassium, and silver, are tending to a maximum rotation of between 14° and 15°; and, as the change in all of them with increasing dilution is comparatively slight, 14·5° may be taken as the molecular rotation of the lactic acid ion. The results of our observations are quite in accordance with the law of Oudemans, and the theory of electrolytic dissociation. In this group of salts, Guye's theory of the influence of mass on the rotation of a substance finds but little confirmation, because the table of curves shows that in the most concentrated solutions which are comparable for the four salts, that is ½ normal, where there must be a very considerable number of undissociated molecules present, there is not 2° of difference in the rotation produced by such different masses as 7, 23, 39, and 108. Increase of mass increases the rotation slightly, but this increase is insignificant. Assuming, as is generally done at present, that the only factors existing in these solutions, which can influence the rotation, are the lactic ions and the whole molecules, it follows that the rotation of the latter must be less than that of the former—except in the case of the silver salt, the rotation of which decreases slightly with dilution—and that the rotation of the whole molecule can differ but little from that of the ion. It may however be pointed out that the same observed results could be accounted for by assuming that the rotation of the whole molecule is greater than that of the ion, and that a not inconsiderable number of complex molecules whose rotation is less or even of opposite sign are present in the more concentrated solutions. This supposition, which seems to us probable, will be discussed later under the alcoholic solutions.

In the second group of salts, comprising those of barium, strontium, and calcium, those of barium and strontium are quite normal, and the influence of mass is found affecting the rotation but slightly. Reference to the table of curves shows that they too in dilute solution approach the same maximum as the former group, that is, the value 14·5° for the molecular rotation. With the calcium salt, however, the case is entirely different, notwithstanding the fact that its degree of electrolytic dissociation cannot be assumed to be very much less than that of the barium and strontium salts. Nor can the difference of mass alone be taken as a sufficient explanation of its apparently anomalous behaviour, because, firstly, its rotation does not approach the maximum by dilution; and, secondly, there is the same difference of mass between the barium and strontium as between the strontium and calcium salts, although the strontium salt shows no tendency to this abnormal rotation.

In the third group of salts, namely, those of magnesium, zinc, and cadmium, what appears at first sight to be the influence of mass is much more striking. The rotation in normal solutions increases with the molecular weight to a very considerable extent, the difference being about 5·5° for a difference of mass of 88 between magnesium and cadmium. The curve of the magnesium salt rises normally, and as the degree of dissociation of a magnesium salt even in N/10 solution is far from complete, it probably, with continued dilution, approaches the maximum value. The same may be said of the zinc salt. The values obtained for the rotations of these two salts would seem to be explicable on the assumption that the rotation of the whole molecule is much less or of opposite sign to that of the ion. From our determinations of the freezing points of their solutions, however, it appears that the amount of dissociation in the zinc salt is only between 30 and 40 per cent., whilst its rotation has already nearly reached the maximum value; and, from the difference between the $\frac{2}{5}$ N and the N/10 solutions, an increase of about 15 per cent. in dissociation is found to produce an increase of 3° in rotation—a rate of increase which would carry the final value of the ionic rotation as found from the zinc salt far beyond that found from the salts of the alkalis. The same reasoning applies to the cadmium salt, in which, although we have not determined the amount of dissociation, it can scarcely far exceed that of the zinc salt. Now, if the rotation of the whole molecule of these salts is even slightly less than that of the ion, the two could only become equal at infinite dilution, and the rate of increase, judging from the amount of dissociation, should be much slower than experiment has shown to be the case. If the two were equal, the rotation should not change with concentration. Consequently our results seem to prove that, in these salts, the rotation of the whole molecule must be greater than that of the ion, and that some other factor must be introduced to account for the diminution of rotation with increase of concentration. Now Arrhenius has assumed the existence of complex molecules to account for the differences found in the salts of this group of metals, between the amount of dissociation determined by electrical conductivity and by depression of freezing point, and it seems highly probable that in the solutions of zinc and cadmium lactates—and probably of others also—the decrease of rotation is due to the presence of complex molecules which rotate the plane of light to a less extent or even in an opposite direction to the simple molecule or the ion. This supposition would seem to be supported by the well-known fact that the lactates show a great tendency to form double salts, not only with other lactates, but also with other organic and inorganic substances.

The presence of complex molecules in solution having a low or negative rotation is also confirmed by the values found for the zinc ammonium lactate. Although it contains the salt of an alkali, and its rotation might therefore be expected to be a mean between that of zinc lactate and ammonium lactate, we find, on the contrary, that in normal solution its rotation is much lower even than that of zinc lactate, whilst its curve rises more rapidly, and finally cuts that of zinc lactate at the concentration of N/10, showing that in dilute solution the salt is slowly dissociated into zinc lactate and ammonium lactate.

Alcoholic and Alcoholic Aqueous Solutions.—The observations contained in Tables II and III which were made with the view of determining the effect of other solvents on the optical activity of the lactates, seem to us to show that not only in the three salts above mentioned, but also in others—possibly in all—the decrease of rotation with increased concentration is due to the presence of complex molecules in solution, of lower, and in some cases, at all events, of opposite rotatory power to the ion.

Sodium l-*lactate in Ethylic Alcohol.*—From the curve in which the molecular rotations are plotted as normals, and the concentrations as abscissæ, it is at once evident that, in very concentrated alcoholic solutions, this salt possesses a rotation opposite to that which it has in water, and, passing over to the same sign on dilution, finally acquires a value much greater than that possessed by the salt in the corresponding aqueous solution, or even than that indicated by the curve as the true ionic rotation. A determination of the molecular weight of the salt by Beckmann's boiling-point method gave the following result:—Weight of salt determined by sodium estimation, 0·6349 gram; weight of alcohol, 21·31 grams; rise of boiling point, 0·260°, from which follows the molecular weight, 132; calculated molecular weight, 112. The fact of too high a value being found for the molecular weight is quite in accordance with the polarimetric observations, for the curve shows no indication of having yet attained a maximum. Unfortunately, the observed angle was becoming too small to permit of our using greater dilutions with the same accuracy. We are forced to conclude, therefore, that the rotation of the whole molecule of sodium lactate is greater than that of the ion, and that even in such a dilute aqueous solution as N/10 there is a not inconsiderable number of complex molecules present. The presence of such molecular aggregates in the more concentrated solutions is further indicated by the striking change of activity which they undergo with change of temperature. Thus, a normal solution giving in a 100-mm. tube a rotation of +15′ at 17°. gave at −2° a rotation −4′; another, of concentration 9·3, giving at 3° a rotation of −3′, gave at 11° a rotation of +10′ in a 400-mm. tube. When an aqueous solution of the sodium salt is diluted with ethylic alcohol, it is seen from Table III (p. 631) that the rotation increases more rapidly than when diluted with water, and finally becomes nearly equal to that of the salt in pure alcohol.

Potassium d-*lactate in Ethylic Alcohol.*—The dilute solutions of this salt show the same high rotation as the sodium salt, and the same results are obtained by adding alcohol to a normal aqueous solution, the molecular rotation in a N/20 solution of the latter being 22·5°, and that of the sodium salt 23°. From our observations on concentrated solutions, it would appear either that the potassium salt shows less tendency to form molecular aggregates than the sodium salt, or that these aggregates are possessed of a rotation in the same sense as the ion. The same conclusion is also indicated by a comparison of our observations on the concentrated aqueous solutions of these salts, where the curve of the potassium salt falls more slowly than that of the sodium salt.

Lithium lactate in Aqueous Alcohol.—Active lithium lactate is insoluble, or nearly so, in pure alcohol, but solutions prepared by adding alcohol to a normal aqueous solution, gave results, as will be seen from the table, corresponding to those obtained with the sodium and potassium salts. Aqueous alcoholic solutions of the calcium, magnesium, zinc, and cadmium salts were also examined by taking readings quickly before the salt had time to crystallise. All of them show a great tendency for the rotation to become of opposite sign in alcoholic solution, and a comparison of the rotations of the calcium and strontium salts is specially interesting. The strontium salt, in water, has a much greater rotation than the corresponding solution of the calcium salt; in aqueous alcohol, its rotation is small and of opposite sign, whilst that of the calcium salt is also reversed in sign, but much more so by the addition of alcohol. This shows clearly that the low rotation of the latter salt is not due to the actual feeble activity of its individual molecule, but to the presence of two active factors, one of which slightly predominates in aqueous, the other in alcoholic solution. The one factor may consist, as in the sodium salt, of whole molecules and ions whose high positive activity is reduced by the opposite rotation of molecular aggregates; or, in the calcium salt, the whole molecules and aggregates may combine to reduce the ionic rotation. This explanation applies equally well to the decrease of rotation observed with increase in the concentration in the barium and strontium salts.

Potassium d-*lactate in a Mixture of Methylic and Ethylic Alcohols.*—The normal solution, whose rotation is quoted below, was prepared by diluting to 25 c.c., with methylic alcohol, 10·43 c.c. of an ethylic alcohol solution containing 3·2025 grams of the salt. The more dilute solutions were prepared from this by further addition of methylic alcohol.

	N.	$\frac{1}{5}$N.	$\frac{1}{10}$N.
c	12·81	2·562	1·281
α	−7·02°	−1·85°	−0·89°
$[\alpha]_D \frac{M}{100}$	−17·54°	−23·10°	−22·23°

The numbers quoted for the molecular rotation show that, by dilution, it reaches a maximum at N/5, after which it appears to fall slowly again, as one would expect, towards the value obtained for the ionic rotation, and a comparison with the table of rotations in ethylic alcohol shows that the values found in the mixture of alcohols are greater than those found in pure ethylic alcohol for corresponding concentration. Both of these observations are quite in accordance with the views at present held as to the solvent action of alcohols. Methylic alcohol possesses a greater power of breaking down molecular complexes than ethylic alcohol, consequently the point at which the number of simple molecules predominates over that of the ions and aggregates is arrived at and passed sooner in methylic than in ethylic alcohol.

The chief conclusions to be drawn from the foregoing observations and considerations are that, although by sufficient dilution a value can be found to represent the rotation due to the ion alone, in more concentrated solutions other factors besides simple molecules appear, representing probably different degrees of aggregation in the different salts; and that these aggregates are decomposed into their constituent molecules and ions to a far different degree by different solvents. In this connection, we may refer to Walden's observations on the rotation of α-bromocamphoric acid and its barium salt when dissolved in water, and in aqueous acetone (*Zeit. physikal. Chem.*, 1894, **15**, 196). In aqueous solution, he finds that a difference of 20 per cent. in the degree of dissociation of the acid, as determined by conductivity, produces a difference of 14° in molecular rotation, whilst in aqueous acetone, a decrease of only 2 per cent. in dissociation lowers the molecular rotation through 17°. In the barium salt, for a difference of 5 per cent. in dissociation, the molecular rotation is decreased by only 1° in aqueous solution, whereas, in aqueous acetone, a lowering of 3 per cent. in the degree of dissociation, produces a fall of 27° in molecular rotation. It seems therefore necessary to conclude either that determinations of the electrical conductivity in these acetone solutions gives no measure of the degree to which a substance is dissociated, or that the great fall on dilution above referred to is due to more than the dissociation of the substance into ions. The apparently contradictory results could be accounted for in the same way as we have sought to explain those of the lactates, only in this case the complex molecule must have a rotation higher than that of the ion.

Comparison of the Freezing Points of Solutions of the Active and Inactive Lactates.

The question of the existence of racemoïd compounds in solution is a subject of considerable interest, both on account of its bearing on the practical methods of resolving them into their active components and also in connection with the wider question of the chemical nature of such compounds in general. Investigation in the subject has been chiefly confined hitherto to racemic acid. The thermo-chemical experiments of Berthelot, Jungfleisch, and Jahn, the determinations of the conductivity by Ostwald (*Zeit. physikal. Chem.*, 1889, **3**, 371), and of the specific volume by Marchlewski (*Ber.*, 1892, **25**, 1556), of solutions of racemic and of the tartaric acids, have proved that, in dilute solution, at all events, racemic acid is resolved into its components. Marchlewski's experiments, however, indicated that in more concentrated solutions (10—14 per cent.) some racemic acid probably remained undecomposed, and freezing point determinations by Raoult (*Zeit. physikal. Chem.*, 1887, **1**, 186) led to the same result Similar experiments by the latter on the sodium ammonium salts showed that, even in 13 per cent. solutions, the racemate was entirely decomposed.

We have applied Raoult's method to the lithium, strontium, and barium lactates. The results of a comparison of the freezing points of solutions of similar strength, of one of the active forms, and the inactive form of each of these salts are contained in Table V. The solutions of the active salts used were some of those whose freezing points have been already quoted, the letters *d* and *l* indicating the sign of activity of the acid from which the salt was made. The solutions of the inactive salts, indicated in the table by the letter *i*, were prepared in the same manner as the active solutions; P being calculated, as already stated, from the specific gravity and known concentration. The inactive calcium and strontium salts were analysed, and found to have the composition commonly assigned to them. The inactive lithium lactate, which does not seem to have been previously prepared, forms crystalline scales of pearly lustre, not distinguishable from the active isomeride; the former crystallises, however, in the anhydrous state, the latter, apparently, as already stated, with $\frac{1}{2}H_2O$. Estimations of lithium in the salt dried in air and at 120° gave the numbers 7·00 and 7·19 per cent. respectively, the calculated percentage for the anhydrous salt being 7·29.

TABLE V.—*Freezing Points of Solutions of Active and Inactive Lactates.*

Lithium Lactate.

c.		Δ.	*d* 13°/4°.	P.	$\frac{\Delta}{P}$.
d.	N......	3·927°	1·0386	10·185	0·386
i.		3·929	1·0382	10·189	0·386
			Calcium Lactate.		
i.	$\frac{1}{5}$N.....	—	1·0107	—	—
d.		—	1·0108	—	—
			Strontium Lactate.		
i.	N......	1·889°	1·0784	14·038	0·135
d.		1·866	1·0783	14·039	0·133
			Barium Lactate.		
i.	N......	2·050°	1·1010	16·6930	0·123
d.		2·187	1·1017	16·6808	0·131
i.	$\frac{2}{5}$N.....	0·888	1·0113	6·4397	0·138
d.		0·925	1·0116	6·4378	0·144
i.	$\frac{1}{5}$N.....	0·460	1·0204	3·1854	0·144
d.		0·487	1·0205	3·1850	0·153
i.	$\frac{1}{10}$N....	0·234	1·0098	1·5844	0·148
d.		0·216	1·0100	1·5841	0·155

An inspection of the table shows that, in the case of the normal solutions of lithium and strontium lactates, the specific gravities and co-efficients of depression Δ/P of the active and inactive forms are practically identical; no freezing points were taken with the inactive calcium lactate, but the specific gravity of its N/5 solution is identical with that of the corresponding solution of calcium *d*-lactate. It appears therefore that, in solutions of these salts of the concentration mentioned, the racemoid salt undergoes complete dissociation into its active components. In the case of the barium lactates, the active salt has in each solution a somewhat higher co-efficient of depression than the inactive salt, which would indicate that the racemoid salt in this case is not completely dissociated, but, as the specific gravities show no corresponding differences, and as the differences of depression do not diminish in the more dilute solutions, we are inclined to think that the differences in question are to be attributed, in all probability, to an error in taking the freezing point of the water.

United College of St. Salvator and St. Leonard
University of St. Andrews.

LXIX.—*The Interaction of Sulphur and α-Nitronaphthalene.*

By Armand Herzfelder, Ph.D.

I have to thank Professor Ramsay for having kindly directed my attention to the fact that on heating a mixture of sulphur and α-nitronaphthalene a green substance is produced which has not hitherto been investigated; I have studied this product, and although the results obtained are not final I give some of the points of interest that have been determined.

Every mixture of sulphur and α-nitronaphthalene (excluding those with more than 80 per cent. of sulphur, when a hard brown mass is formed) when melted, acquires a light green colour, and at above 300° a vigorous action sets in, which continues, without further heating; sulphur dioxide and nitronaphthalene vapour being evolved, and a black mass left. When the sulphur is less than 25 per cent. the greater part of the nitronaphthalene remains unchanged, but as this excess is more readily separated from the product than excess of sulphur, and as the action then begins at about 240°, it is advantageous to work with these proportions.

As a rule, 150 grams of nitronaphthalene were well mixed with 30 grams of flowers of sulphur, and heated in an Erlenmeyer flask over a bare flame; as soon as the mixture began to boil, the flame was removed. On cooling, the black mass was pulverised and boiled with alcohol to remove the excess of nitronaphthalene and any unchanged sulphur; the residue was then heated with chloroform, and the filtrate rejected, as it contained, along with some of the green product, the greater part of the free sulphur. The residue was now boiled with large quantities of chloroform as long as it gave a dark green solution, filtered while still hot, and the solution precipitated with alcohol; this operation was repeated three times. The precipitate was collected and boiled with successive quantities of alcohol; the first extract was colourless, containing sulphur only, but after the third treatment the solution was pale green, and the extraction was then discontinued.

In this way a dark green amorphous powder was obtained, insoluble in ether, alcohol, acids, and alkalis, but soluble in liquids which dissolve sulphur easily, such as chloroform, carbon bisulphide, phenol, benzene, nitrobenzene, and aniline. It is not volatile with steam, and I did not succeed in subliming it, as it decomposed soon after melting, even in a vacuum. To purify the original substance, other methods were used such as fractional precipitation with alcohol from the nitrobenzene solution, precipitation with alcoholic potash from its solution in phenol, and also by shaking with colourless ammonium sulphide. I succeeded in reducing the amount of sulphur in the product from 27 per cent. to 19·5 per cent. As all my efforts to obtain the substance in a crystalline state were unsuccessful, I accepted this amorphous substance as pure. It melted at 155°, and the sp. gr., determined by the method of suspension, was 1·225, whether the substance had been previously melted or not. The following numbers show the slight solubility of the compound.

Solvent.	Temperature.	Percentage solubility.
Chloroform.............	61°	0·217
„	12	0·201*
Amylic acetate..........	12	0·313
Nitrobenzene...........	12	2·150

It is difficult to recover the substance from its solution in nitrobenzene.

Perhaps the most interesting point with regard to this compound is that it is free from nitrogen. This, so far as I know, is the first instance observed of the total elimination of the NO_2 group by heating with sulphur. A sulphur determination was made.

0·1040 gave 0·1480 $BaSO_4$. S = 19·54.

Calculated for $C_{10}H_6S$, 20·2 per cent.

The molecular weight as determined from the elevation of the boiling point of chloroform was 152. As the elevation was small, owing to the sparing solubility of the substance, this number is in sufficiently close agreement with the molecular weight of $C_{10}H_6S$, which is 158.

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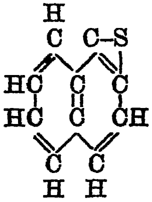
* The solubility of sulphur in chloroform at 22° is 1·2 per cent.

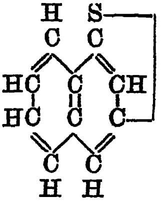
It was natural to suppose that if one sulphur atom were substituted for the group NO_2, the free valency of the sulphur would be satisfied by hydrogen, so that the sulphur would be in the condition in which it exists in the thioalcohols or thiophenols The reactions of the green substance, however, do not confirm this supposition. In contradistinction to the mercaptans, it has no odour, does not react with mercuric oxide, and gives no precipitate with mercuric chloride or lead acetate.

The complete neutrality of the compound, and the results of the oxidation and bromination detailed further on, led me to believe that the second valency of the sulphur is also satisfied by one of the naphthalene carbon atoms, that is, the compound has the formula $C_{10}H_6S$. On oxidation with nitric acid, I obtained, amongst other products, phthalic acid, which shows that the sulphur is bound only to one of the naphthalene rings. Of the three possibilities

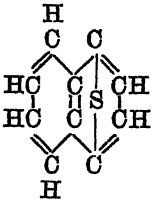
I.



II.

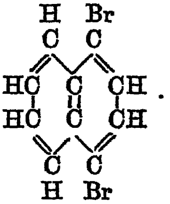


III.

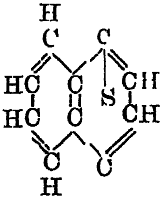


the bromination showed the third formula to be the most probable.

To a concentrated solution of the green compound in carbon bisulphide, a great excess of bromine was added, and the mixture allowed to remain for two hours; the excess of bromine was then removed with dilute potash, and the carbon bisulphide by evaporation in a vacuum. The brown residue was extracted with ether, and the ethereal solution, concentrated, was poured into cold alcohol; the precipitate formed was proved to be the dibromonaphthalene melting at 85°, and having the constitution



This result entitles me to ascribe to the green compound the formula of an *αα'*-thionaphthalene. The relation to thiophen is seen from the following formula.



Unlike this substance it gives no reaction with the diphenols.

Bromination

A dilute solution of bromine in carbon bisulphide was added to the thionaphthalene dissolved in the same solvent, and the mixture allowed to remain 24 hours. On evaporating the carbon bisulphide, there remained, besides *αα′*-dibromonaphthalene, a brown mass which, on treatment with ether containing bromine dissolved in it, yielded a green, amorphous substance almost insoluble in alcohol or in pure ether. This proved to be a monobromothionaphthalene, or probably a mixture of isomeric bromo-derivatives, for, although it contained the calculated quantity of bromine and sulphur, it had no well-defined melting point. The excess of bromine and ether was expelled by heating first on the water bath and then in a vacuum, the residue washed successively with ether, alcohol, and water, and finally dried in a desiccator.

0·0531 gave 0·0514 $BaSO_4$. S = 13·3.
0·0319 „ 0·0253 AgBr. Br = 33·7.
Calculated for $C_{10}H_5BrS$. S = 13·5; Br = 33·8 per cent.

The position of the bromine atom in the molecule has not been ascertained.

Sulphonation.

Thionaphthalene was added to concentrated sulphuric acid, and the mixture left for 12 hours with occasional shaking; the black mass was then poured into water, collected, and washed until the washings no longer gave a precipitate with barium chloride. The resulting thionaphthalenesulphonic acid being insoluble in water was dissolved in boiling aqueous potash, the solution filtered, and the free alkali neutralised with hydrochloric or acetic acid. Barium chloride and lead acetate gave precipitates of the barium and lead salts of the sulphonic acid, which could only be removed from the filter when wet. The lead salt, when dry, was a reddish-brown, amorphous powder, and the barium salt a gray powder. As no further purification of these salts could be effected, the numbers obtained on determining the metals in them were only approximate, being somewhat below the theoretical.

Nitration.

Thionaphthalene, when boiled with nitric acid, gave a black solid mass, and the acid became red. On extracting with ether, a red solution was obtained, which was mixed with alcohol; the ether was then evaporated off on the water bath, and the alcoholic solution precipitated with water. A red substance was thus obtained melting at 48°, and containing both sulphur and nitrogen.

The black mass was dried and shaken up with chloroform; the addition of alcohol to the chloroform solution precipitated a black substance which melted at 98—105°, and contained nitrogen and sulphur.

Besides these products, I obtained nitrobenzene, detected by Brunner's reaction (*Zeit. anal. Chem.*, 1881, 390), and traces of phthalic acid.

It is extremely difficult to obtain these derivatives of thionaphthalene in large quantity or in a state of purity, as the thionaphthalene itself is very inert and total decomposition often takes place on heating. I am at present engaged in the preparation of various other derivatives in the hope of more closely characterising thionaphthalene and of confirming the formula suggested.

Budapest.

LXX.—*Acid Compounds of some Natural Yellow Colouring Matters.*

By A. G. Perkin, F.R.S.E., and L. Pate.

In a previous communication by one of us, in conjunction with J. J. Hummel (*Ber.*, 1882, 15, 2337), it was shown that hæmateïn and brazilein, the colouring matters of logwood and brazilwood, yielded peculiar compounds with mineral acids. Thus, from hæmateïn, $C_{16}H_{12}O_6$, there was obtained isohæmateïn sulphate, $C_{16}H_{11}O_5{\cdot}SO_4H$, and isohæmateïn chlor- and brom-hydrins, $C_{16}H_{11}O_5Cl$ and $C_{16}H_{11}O_5Br$. These substances, on treatment with water, are decomposed with elimination of acid, the first product formed in the case of the sulphuric acid compound being a basic sulphate,

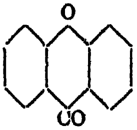
$$(C_{16}H_{12}O_6)_2,C_{16}H_{11}O_5{\cdot}HSO_4.$$

Further, by treating the chlor- or brom-hydrin with silver oxide, a substance, isohæmateïn, $C_{16}H_{12}O_6$, was obtained, which, though isomeric with hæmatein, differed considerably from it in dyeing and other properties. Brazileïn behaved similarly. It was therefore evident that, by the action of mineral acids on these colouring matters, some change other than the mere formation of an acid compound had taken place.

In continuation of this work, it appeared desirable to study in a similar manner the action of acids on the natural yellow dyes. Although it seems to have been already known that some of these substances give colour reactions with some of the mineral acids, no attempt has been made to study this action. The only statements bearing on this subject which we have found appear in Gmelins's *Handbook of Chemistry.* "Warm concentrated hydrochloric acid colours quercetin orange to brown-yellow" (Regaud, **10**, 492). "When a solution of quercetin in acetic acid is saturated with hydrochloric acid gas only a trace is decomposed, the rest acquiring an orange-yellow colour" (Hlasiwetz). "According to Chevreul, luteolin unites with acids" (**9**, 29). "Morin dissolves in oil of vitriol with a dark brown-yellow colour, the solution deposits a red body when warmed or left at rest."

According to the recent researches of Kostanecki (Kostanecki and Tambor, *Monatsh.*, 1895, **15**, 1) on gentisin, the colouring matter of gentian root, of Schunck and Marchlewski on datiscetin from *Datisca cannabina* (*Annalen*, 1894, **277**, 261), and of Herzig (*loc. cit.*), certain of the natural yellow colouring matters can be divided into two classes, in that they are either derivatives of dipheno-γ-pyrone or of a phenylated pheno-γ-pyrone,

I.



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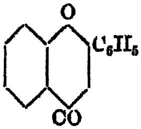

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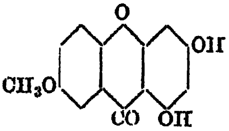
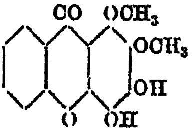
To the former class belong gentisin, prepared artificially by Kostanecki and Tambor (*loc. cit.*),



;

and datiscetin, which, according to Schunck and Marchlewski (*loc. cit.*), is thus represented



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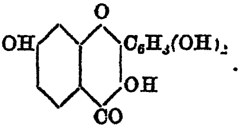
Fisetin, quercetin, rhamnetin, and rhamnazin (quercetin mono- and di-methyl ethers), and chrysin (Kostanecki, *Ber.*, 1893, **26**, 2901) belong to the second class, in which also most probably should be included morin and luteolin, the colouring matters respectively of old fustic and weld. From a study of its decomposition products, Herzig (*Ber.*, 1895, **28**, 293) considers fisetin to have the following constitution.



There also exists a third class of allied substances, of which maclurin, the second colouring matter of old fustic, and catechin, the chief constitutent of catechu, are typical.

The former is usually regarded as a benzophenone derivative.

In the present communication, we have confined ourselves to the study of the action of acids on the members of the second and third classes, and all that are above enumerated have been examined, with the exception of chrysin.

Preliminary experiments were carried out with the following result When boiled with hydrochloric or hydrobromic acids, quercetin, fisetin, and morin yielded orange-red to scarlet crystalline compounds, very readily decomposed by water; they were, however, not acted on when similarly treated with dilute sulphuric acid. On the other hand, rhamnetin and rhamnazin were practically not altered by this treatment. By treating with acids solutions of these colouring matters in glacial acetic acid, more satisfactory results were obtained, the presence of water in quantity being thus avoided.

Quercetin

In order to prepare this substance from quercitron bark (*Quercus tinctoria*), advantage was taken of a method devised by Dr. W. H. Perkin (private communication), and used by him some years ago for its manufacture. Quercitron bark dust is washed with salt solution to remove impurities, and then extracted with cold dilute ammonia. The extract, when neutralised with dilute sulphuric acid, deposits a brown amorphous precipitate containing little or no colouring matter; this is filtered off, and the clear lemon-yellow solution which contains the glucoside, quercitrin, is acidified and boiled, when crystals of quercetin soon begin to separate; these are collected while the mixture is still warm, in order to prevent their contamination with a brown flocculent matter which usually separates out on further cooling. The product consists of almost chemically pure quercetin, and this can be further purified by recrystallisation from dilute alcohol, or more rapidly by extracting with a mixture of ether and chloroform; on evaporating this extract, crystals of pure quercetin separate, as it is practically insoluble in chloroform.

Quercetin Sulphate.—To a boiling saturated solution of quercetin in acetic acid, a few drops of sulphuric acid were added, which turned the liquid orange coloured, and on cooling it deposited a glistening mass of hair-like needles of the same tint; these were collected, washed with acetic acid, and dried at 100°. If quercetin be made into a thin paste with boiling acetic acid, and sulphuric acid be then added, a similar result is obtained without apparent solution of the quercetin. On analysis, the following numbers were obtained.

0·1558 gave 0·2578 CO_2 and 0·0425 H_2O. C = 45·12; H = 3·03.
$C_{15}H_{10}O_7,H_2SO_4$ requires C = 45·00; H = 3·00 per cent.

This substance, when treated with water, is quantitatively decomposed into quercetin and sulphuric acid, as the following results show.

0·4097 gram, standing in water, gave a yellow product, which was collected, washed, and dried at 160°. It weighed 0·3088 = 75·37 per cent. The filtrate yielded 0·2427 $BaSO_4$; S = 8·13 per cent
$C_{15}H_{10}O_7,H_2SO_4$ requires $C_{15}H_{10}O_7$ = 75·5; S = 8 per cent.

The yellow product, dried at 160°, was analysed.

0·1145 gave 0·2511 CO_2 and 0·0372 H_2O. C = 59·80; H = 3·61.
$C_{15}H_{10}O_7$ requires C = 59·60; H = 3·31 per cent.

Quercetin sulphate is slowly decomposed on exposure to moist air, with formation of quercetin and sulphuric acid. It is sparingly soluble in boiling acetic acid, but cannot be recrystallised from this solvent without undergoing decomposition. Boiling acetic anhydride dissolves it readily, forming a colourless solution, which apparently contains an acetyl derivative of quercetin. When strongly heated, it is carbonised, with evolution of sulphurous acid, a small quantity of a crystalline sublimate being simultaneously formed.

Quercetin hydrobromide can be readily prepared by the addition of fuming hydrobromic acid to a boiling solution of quercetin in acetic acid, or to quercetin suspended in the same liquid. The product is washed with acetic acid and dried at 100°. Analysis gave the following result.

0·1173 gave 0·2033 CO_2 and 0·0300 H_2O. C = 47·26; H = 2·84.
$C_{15}H_{10}O_7,HBr$ requires C = 47·00; H = 2·87 per cent.

It consists of a glistening mass of orange-yellow needles readily decomposed by contact with water.

0·3680 thus treated gave 0·2925 quercetin and 0·1814 AgBr, corresponding with $C_{15}H_{10}O_7$ = 79·48. Br = 20·97.

$C_{15}H_{10}O_7,HBr$ requires $C_{15}H_{10}O_7$ = 78·85; Br = 20·63 per cent.

It is sparingly soluble in acetic acid, but cannot be recrystallised without decomposition.

Quercetin hydrochloride, prepared in a similar manner, closely resembles the hydrobromic acid compound. A sample dried at 100° yielded on analysis C = 57·6; theory requires C = 53·17, and this result was accounted for by the fact that when heated to this temperature it is gradually decomposed, with evolution of hydrogen chloride and formation of quercetin.

Quercetin hydriodide, $C_{15}H_{10}O_7,HI$, forms a glistening mass of orange needles having similar properties to the above compounds.

These results corroborate those of Herzig (*Monatsh.*, 1891, **12**, 172), in that they show quercetin to have the formula $C_{15}H_{10}O_7$, and not $C_{24}H_{16}O_{11}$, as previously supposed.

Fisetin.

To prepare this substance, young fustic (*Rhus cotinus*, L.) was extracted with boiling water, and the extract treated with lead acetate solution. The lead compound of the colouring matter thus formed was collected, made into a thin paste with water, and in a fine stream run into boiling dilute sulphuric acid. After removal of the lead sulphate, the dark coloured filtrate on cooling deposited a semi-crystalline, brownish mass, which was collected and purified by crystallisation from dilute alcohol.

Fisetin Sulphate, $C_{15}H_{10}O_6,H_2SO_4$.—To a pasty mass of fisetin and boiling acetic acid, sulphuric acid was added, and the scarlet, crystalline product thus obtained collected and washed with acetic acid. Owing to the somewhat ready solubility of this substance in acetic acid, considerable loss occurs during the washing. This may be avoided to some extent by alternately washing, and draining the mass upon a porous tile. On analysis, the following numbers were obtained.

0·1326 dried at 110° gave 0·2282 CO_2 and 0·0385 H_2O. C = 46·93. H = 3·22.

$C_{15}H_{10}O_6,H_2SO_4$ requires C = 46·87; H = 3·12 per cent.

It forms a scarlet glistening mass of fine needles, considerably more soluble in acetic acid than the corresponding quercetin compound. Water converts it into fisetin and sulphuric acid.

0·3909 gave 0·2915 fisetin and 0·2536 $BaSO_4$. $C_{15}H_{10}O_6$ = 74·57; S = 8·88.

$C_{15}H_{10}O_6,H_2SO_4$ requires $C_{15}H_{10}O_7$ = 74·48; S = 8·33 per cent.

Fisetin hydrobromide, $C_{15}H_{10}O_6,HBr$, and *hydrochloride*, $C_{15}H_{10}O_6,HCl$, are obtained as fine orange-coloured needles. On heating to 100° they are decomposed, leaving fisetin. *Fisetin hydriodide*, $C_{15}H_{10}O_6,HI$, closely resembles the above compounds.

Herzig (*Ber.*, 1895, **28**, 293) has assigned to fisetin the formula $C_{15}H_{10}O_6$, with which the above results agree.

Morin.

Morin, which, together with maclurin, is contained in old fustic (*Morus tinctoria*), is best obtained by extracting this dyestuff with boiling water, the extract thus obtained depositing, on cooling, impure morin. For some quantity of this product, we are indebted to the kindness of Messrs. Wood and Bedford of Leeds. It was purified by several crystallisations from alcohol and dilute acetic acid.

Anhydromorin sulphate, $C_{15}H_8O_6,H_2SO_4$, is readily formed by the addition of sulphuric acid to a boiling solution of morin in acetic acid; the orange-red crystalline mass deposited on cooling was collected, washed with acetic acid, and dried at 110°.

0·1636 gave 0·2810 CO_2 and 0·0450 H_2O. C = 46·84; H = 3·05.
0·1457 gave 0·2507 CO_2 and 0·0402 H_2O. C = 46·99; H = 3·07; S = 8·38.
$C_{15}H_8O_6,H_2SO_4$ requires C = 47·11; H = 2·62; S = 8·32 per cent.
$C_{15}H_{10}O_7,H_2SO_4$ requires C = 45·00; H = 3·00 per cent.

That morin has the formula, $C_{15}H_{10}O_7$, and not $C_{15}H_8O_6$ is evident from the analysis of its compounds with hydrogen bromide and chloride described below. The sulphuric acid compound of morin, therefore, differs from those of quercetin and fisetin previously described, in that one molecule of water is removed during its formation. When treated with water, however, it is reconverted into morin, sulphuric acid being formed. The morin so produced was analsyed.

0·1077 gave 0·2335 CO_2 and 0·0345 H_2O. C = 59·13; H = 3·55.
$C_{15}H_{10}O_7$ requires C = 59·60 and H = 3·31 per cent.

The crystals of anhydromorin sulphate are considerably larger and of much greater beauty than the corresponding derivatives of fisetin and quercetin. It is almost insoluble in acetic acid.

Morin hydrobromide forms a glistening mass of long orange-coloured needles, almost insoluble in acetic acid. On analysis

0·157 gave 0·272 CO_2 and 0·0410 H_2O. C = 47·24; H = 2·90.
0·149 „ 0·2568 CO_2 and 0·0386 H_2O. C = 47·00; H = 2·87.
0·5168 „ 0·2592 AgBr. Br = 21·34.
$C_{15}H_{10}O_7,HBr$ requires C = 47; H = 2·84; Br = 20·63 per cent.

It is readily decomposed by water into morin and hydrobromic acid.

Morin hydrochloride closely resembles the preceding compound, but is somewhat less stable at 100°. In order to submit this compound to analysis, the freshly prepared substance, after washing with acetic acid, was well pressed, treated with water, and the morin produced dried at 160°. It weighed 0 2285 gram. The filtrate was neutralised, evaporated to dryness, ignited, and the amount of chlorine present in the residue determined. It yielded 0·105 AgCl.

Morin = 89·21 per cent. Cl = 10·14 per cent

$C_{15}H_{10}O_7,HCl$ requires $C_{15}H_{10}O_7$ = 89·21. Cl = 10·49 per cent.

Morin hydriodide, $C_{15}H_{10}O_7,HI$, closely resembles the above compound.

The ready production of these compounds, together with their sparing solubility in glacial acetic acid, and also the fact that maclurin yields no compounds with acid, provides a method for greatly facilitating the purification of morin. The crude morin is crystallised twice from alcohol, the product suspended in acetic acid and converted into the hydrogen bromide compound; this is collected, washed with acetic acid until the filtrate is nearly colourless, suspended in a little boiling acetic acid and the mixture treated with its own volume of boiling water. A clear solution is thus obtained which, on cooling, deposits long, colourless, glistening needles of pure morin.

The study of morin has received but little attention, and consequently there has been some uncertainty as to its molecular weight. Two formulæ have been assigned to it, namely, $C_{12}H_8O_6$ (Hlasiwetz and Pfaundler, *Annalen*, 1863, **127**, 252) and $C_{15}H_{10}O_7$ (Löwe, *Zeit. anal. Chem.*, **14**, 119), both having a similar percentage composition. The above results show that Löwe's formulæ, $C_{15}H_{10}O_7$, must be regarded as correct.

Rhamnetin.

This substance was prepared from Persian berries in the manner described in a previous communication (Perkin and Geldard, this vol. p. 496). If a pasty mass of rhamnetin in boiling acetic acid be treated with a few drops of sulphuric acid, the liquid becomes somewhat yellower, but the suspended rhamnetin remains unaltered. It was at first supposed that it did not form a compound with sulphuric acid, but it was subsequently found that a large excess of sulphuric acid is required. To rhamnetin suspended in boiling acetic acid, sulphuric acid was added drop by drop until it dissolved; the clear solution, on standing, quickly deposited a mass of beautiful, orange-coloured, prismatic needles, sometimes interspersed with unaltered rhamnetin. If this was the case, fresh acid was then added and the mixture again boiled. The product was collected upon glass wool with the aid of the pump, and washed twice with acetic acid; it could not, however, be thoroughly washed with acetic acid, as it was gradually decomposed into sulphuric acid and rhamnetin, this, however, could be avoided by the use of acetic acid containing 25 per cent. of acetic anhydride. The product, drained upon a porous tile which had been previously heated and allowed to cool over sulphuric acid, was left in a dessicator for three or four days before being analysed.

0·1283 dried at 160° gave 0·2195 CO_2, 0·0400 H_2O. C = 46·65; H = 3·46.

$C_{16}H_{12}O_7,H_2SO_4$ requires C = 46·37; H = 3 38 per cent.

By treatment with water, it is decomposed quantitatively into rhamnetin and sulphuric acid.

0·2985 gave 0·2275 rhamnetin, and 0·1792 $BaSO_4$. $C_{16}H_{12}O_7$ = 76·21; S = 8·17 per cent.

$C_{16}H_{12}O_7,H_2SO_4$ requires $C_{16}H_{12}O_7$ = 76·32; S = 7·73 per cent.

Rhamnetin sulphate is exceedingly unstable, becoming pasty on exposure to the air, with formation of sulphuric acid and rhamnetin As is well known, rhamnetin is a quercetin monomethyl ether and has the formula, $C_{16}H_{12}O_7$, with which the above results agree.

No compounds of rhamnetin with hydrogen bromide or chloride could be obtained.

Rhamnazin.

As previously shown, this substance is a quercetin dimethyl ether (this vol., 496), and is contained, together with rhamnetin and quercetin, in Persian berries. Its behaviour towards sulphuric acid closely resembles that of rhamnetin, except that an even larger quantity of sulphuric acid is necessary for the formation of this derivative. On analysis, the following numbers were obtained.

0·1269 gave 0·2244 CO_2 and 0·0435 H_2O. C = 48 24; H = 3·81.

$C_{17}H_{14}O_7,H_2SO_4$ requires C = 47·66; H = 3·74 per cent.

Rhamnazin sulphate is exceedingly unstable, being readily decomposed by contact with glacial acetic acid, and appears also to undergo slow decomposition even when standing over sulphuric acid. It forms a mass of beautiful, scarlet, glistening needles, moderately soluble in cold acetic anhydride. No compounds of rhamnazin with hydrogen chloride or bromide could be obtained.

Maclurin was prepared from old fustic in the usual manner. When acted on with acids by the methods above described, its nearly colourless solution in acetic acid became of an orange tint. No crystalline compounds, however, could be isolated, and we are of opinion that the change of colour, above referred to, is due rather to a decomposition than to any combination of the acid and colouring matter. This appears to be corroborated by the fact that Wagner (*Jahrsber.*, 1851, 420) obtained a substance, rufimoric acid, $C_{16}H_{14}O_9$, (?) by the action of cold sulphuric, or boiling hydrochloric, acid on maclurin.

Catechin.—No acid compounds could be obtained from this substance, its solution in acetic acid being unaffected by the addition of acid. By prolonged action of acid, catechin is converted into a dark red-brown powder (Kraut, Delden, *Annalen*, 1863, **128**, 291), termed catechuretin, $C_{12}H_{30}O_{13}$, in this respect somewhat resembling maclurin.

Curcumin.—While examining the action of acids on the above colouring matters, it appeared of interest to test the behaviour of curcumin when similarly treated, and, for this purpose, a small quantity of it was prepared from turmeric in the usual manner. An acetic acid solution, when treated with sulphuric or hydrochloric acids, acquires a blood-red colour, but no crystalline matter separated on standing. That this coloration, however, was due to the formation of acid compounds appeared probable, for, by treatment with water, a yellow precipitate was formed, which seemed to consist of unchanged curcumin. When boiled with strong aqueous hydrochloric or hydrobromic acids, curcumin is decomposed, with formation of a resinous product.

Summary of Results.

It is shown by this investigation that quercetin and fisetin react readily with sulphuric, hydrochloric, hydrobromic, and hydriodic acids, forming well-defined, crystalline compounds, the composition of which is represented as the addition of 1 mol. of acid to the colouring matter. With hydrobromic, hydrochloric, and hydriodic acids, morin behaves similarly, but differs in that, during the formation of its sulphuric acid derivative, 1 mol. of water is eliminated. No action takes place between rhamnetin or rhamnazin (quercetin mono- and dimethyl-ethers) and the haloïd acids, but with sulphuric acid, compounds are produced, though far from readily. This difference in behaviour must be accounted for by the methoxy-groups they contain.

The acid derivatives of all these colouring matters are almost instantaneously decomposed by water into acid and the original colouring matter, thus showing considerable difference from those produced from hæmatein and brazileïn, which are referred to in the introduction to this paper. Maclurin and catechin do not yield compounds with acids.

Before entering into a discussion of the constitution of these substances, we feel it preferable to study the behaviour of acids towards that class of dyes and allied substances to which gentisein and datiscetin belong.

This investigation will be proceeded with when the necessary raw material is to hand.

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Dyeing Department,
Yorkshire College.

LXXI.—$\beta\beta$-*Dinaphthyl and its Quinones.*

By Frederick D. Chattaway, B.A., Christ Church, Oxford.

It is somewhat remarkable that so little is accurately known of the various possible dinaphthyls. Several substances of the composition, $C_{20}H_{14}$, differing considerably in melting point and physical properties, have been prepared, but the constitution of only one of these, $\alpha\alpha$-dinaphthyl, has been determined. Speculations as to the constitution of the others have been based entirely upon their relative melting points, and indeed the actions by which they have been produced, generally unexpectedly, lead to opposite conclusions.

Lossen first obtained a dinaphthyl (*Annalen*, 1867, **144**, 77) by oxidising naphthalene with manganese dioxide and dilute sulphuric acid, and, by synthesising it from α-bromonaphthalene, showed that it was the $\alpha\alpha$-derivative. Watson Smith (*J. C. Soc.*, 1871, **24**, 1184) prepared a hydrocarbon, melting at 204°, by passing naphthalene vapour through a red-hot iron tube; this he termed isodinaphthyl, and later he obtained it in larger quantity, melting at 187°, by treating in the same way a mixture of the vapours of naphthalene and antimony trichloride. Gladstone and Tribe (Trans., 1882, **41**, 17) obtained a hydrocarbon resembling isodinaphthyl, and melting at 189°, by distilling aluminium α-naphthylate. Roux (*Bull. Soc. Chim.*, 1884, **41**, 379) states that the same compound is formed in considerable quantity when amylic chloride and naphthalene are heated with anhydrous aluminium chloride, but no melting point is given, nor is it stated how it was recognised. A similar hydrocarbon has also been obtained by Bamberger and Chattaway (*Annalen*, 1895, **284**, 74) by heating, with soda lime, an acid derived from picene.

The author has undertaken the investigation of the dinaphthyls with the object of synthesising the $\beta\beta$- and the $\alpha\beta$-modifications by methods which definitely fix their constitution, and of preparing some characteristic derivatives by which they may easily be identified.

The present paper contains an account of the synthesis of ββ-dinaphthyl, of its quinones, and of some closely related derivatives.

ββ-Dinaphthyl is best obtained by the action of sodium on β-chloronaphthalene dissolved in boiling xylene, in presence of a small quantity of ethylic acetate.

$$\begin{array}{c} C_{10}H_7Cl \\ C_{10}H_7Cl \end{array} + Na_2 = \begin{array}{c} C_{10}H_7 \\ | \\ C_{10}H_7 \end{array} + 2NaCl.$$

It is also produced when zinc dust acts on β-diazonaphthalene sulphate dissolved in alcohol. The hydrocarbon can easily be isolated from the products of these actions as it crystallises well and completely from benzene or xylene. It is beautifully crystalline, separating from its solvents, when pure, in large pearly plates, with a slight blue fluorescence. It melts at 183·5°, and boils at 452° under a pressure of 753 mm. When dissolved in glacial acetic acid and oxidised by chromic acid, one or other of two quinones can be obtained according to the conditions under which the oxidation is performed. If the oxidation be effected rapidly in boiling glacial acetic acid, a quinone is produced in almost theoretical amount, whose composition and molecular weight agree with the formula, $C_{10}H_{12}O_2$. This is a yellow, well-crystallised substance yielding a colourless hydroquinone or quinol, on reduction, and dissolving in concentrated sulphuric acid with a very characteristic indigo-blue colour. Its appearance and behaviour lead to the conclusion that it is a para-quinone analogous to α-naphthaquinone [1 : 4].

When this quinone is heated with a solution of potassium hydroxide, one of its hydrogen atoms is displaced by an OK-group, the hydrogen liberated reducing the quinone to a quinol.

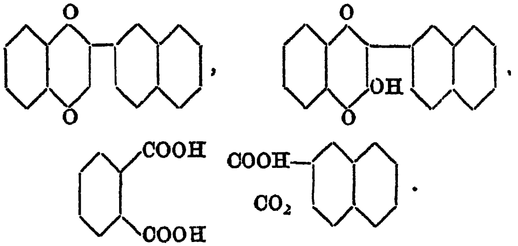
$$C_{20}H_{12}O_2 + KOH = C_{20}H_{11}(OH)_2{\cdot}OK.$$

If this action takes place in presence of air, the two hydroxyl groups are at once oxidised, and the potassium derivative of a hydroxyquinone is formed; on adding an acid to this the hydroxyquinone itself can be obtained,

$$C_{20}H_{11}(OH)_2{\cdot}OK \rightarrow C_{20}H_{11}O_2{\cdot}OK \rightarrow C_{20}H_{11}O_2{\cdot}OH.$$

The hydroxyquinone yields a trihydroxy-derivative on reduction.

This hydroxyquinone, when dissolved in a hot solution of potassium hydroxide and oxidised by a solution of potassium permanganate, yields phthalic acid, carbon dioxide, and an acid, undoubtedly β-naphthoic acid, which gives naphthalene on being heated with soda lime. This seems to show that the quinone is really β-naphthyl-α-naphthaquinone, $C_{10}H_7{\cdot}C_{10}H_5{:}O_2$ [2 : 1 : 4], the displacement of hydrogen by hydroxyl, and breaking down of the molecule taking place as follows:—

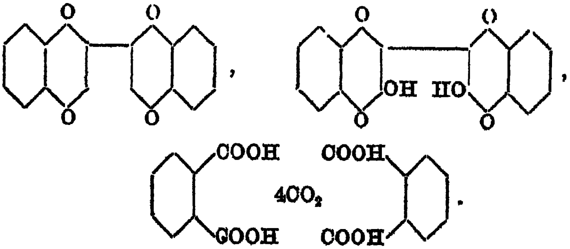


The second quinone, which analysis shows to have the formula $C_{20}H_{10}O_4$, is produced in small quantity if a considerable excess of chromic acid is used in the oxidation, and if the action is prolonged by adding it in small quantities, heating before each addition. It is a yellowish-brown substance which can be easily separated from β-naphthyl-α-naphthaquinone by reason of its sparing solubility in alcohol. It is probably formed by the further oxidation of the naphthyl-naphthaquinone, as it is only obtained in small amount and is always accompanied by tarry decomposition products and by more or less of this substance. It behaves very much like the simpler quinone, its behaviour being modified, apparently, by its containing two naphthaquinone groups instead of one. It dissolves in concentrated sulphuric acid with a bright orange colour, changing rapidly to a deep olive green.

When heated with a solution of potassium hydroxide, it dissolves, two OK-groups displacing two hydrogen atoms, the liberated hydrogen as before reducing the quinone groups to quinol groups.

$$C_{20}H_{10}O_4 + 2KOH = C_{20}H_6(OH)_4(OK)_2.$$

In presence of air, the hydroxyl groups are oxidised, and on adding an acid a dihydroxydiquinone of the composition $C_{20}H_8O_4(OH)_2$ is thrown down. This substance, when dissolved in a boiling solution of potassium hydroxide and oxidised by a solution of potassium permanganate, yields apparently nothing but phthalic acid and carbon dioxide, which makes it probable that the quinone is ββ-di-α-naphthaquinone, $C_{10}H_5O_2{\cdot}C_{10}H_5O_2$ [1 : 2 : 4 1 : 2 : 4], the actions being represented as follows:—



ββ-*Dinaphthyl*, $C_{10}H_7 \cdot C_{10}H_7$.

This hydrocarbon is best prepared by heating sodium with β-chloronaphthalene dissolved in xylene in presence of ethylic acetate. The β-chloronaphthalene is dissolved in about three times its weight of dry xylene, boiling not lower than 150°, somewhat more than the theoretical quantity of sodium and one-twentieth of its weight of ethylic acetate are added, and the liquid heated to brisk ebullition for 30 to 40 hours, small quantities of ethylic acetate being added from time to time and more sodium, of which a considerable excess must be present or the action at the end is very slow.

To obtain the ββ-dinaphthyl, the product is treated with a large excess of boiling xylene and filtered hot. On distilling off the greater part of the xylene, the hydrocarbon is deposited nearly pure as a brownish mud which, on drying, forms a greyish-brown crystalline powder; a further quantity can be obtained by distilling off the xylene from the mother liquor and fractionating the tarry residue. At first, a large quantity of naphthalene distils over, then, more or less unattacked β-chloronaphthalene, and finally, above 360°, ββ-dinaphthyl, mixed, as the temperature rises, with an increasing quantity of a yellow to deep red, resin-like substance. The dinaphthyl can be obtained from the distillate by crystallising it from hot benzene in which the resin appears to be soluble in all proportions. To purify the crude substance, it must be recrystallised repeatedly from benzene after being well boiled with animal charcoal, distilled, and again recrystallised from benzene in order to completely decolorise it—a matter of great difficulty. Although the melting point scarcely changes during these operations, the crystals become larger and larger; at first so small that they can hardly be recognised under the microscope, they finally separate as large glistening plates several centimetres across. Obtained thus, it forms large pearly plates, colourless when absolutely pure, but generally of a faint yellowish-green colour, seen especially when the crystals are large. The yield that can be obtained with care is about 38 per cent. of the theoretical. When ethylic acetate is not added, the yield is much smaller, amounting to only about one-eighth of this.

ββ-Dinaphthyl can also be prepared directly from β-naphthylamine by the action of zinc dust on β-diazonaphthalene sulphate dissolved in alcohol, although no satisfactory method of preparing it thus in quantity has yet been found. To obtain it, the β-naphthylamine is dissolved in about 30 times its weight of alcohol to which 10 times its weight of sulphuric acid has previously been added; the theoretical quantity of sodium nitrate in concentrated solution is stirred in, and the whole allowed to remain for twenty-four hours or so. The solution is then diluted with more alcohol, and an excess of zinc dust mixed with a very little powdered copper sulphate is added gradually, stirring constantly; after this, it is heated on the water bath for some time, then diluted with water, the alcohol completely distilled off, and the solid residue collected, dried, and extracted with hot benzene. From this, the hydrocarbon is obtained by distilling off the benzene and fractionating the residue. At first, naphthalene comes over, then a reddish-brown tarry substance, and finally a reddish-brown resin.

ββ-Dinaphthyl crystallises out on dissolving these tarry and resinous fractions in a little hot benzene and allowing the thick solutions to stand for some hours. A yield of about 3 per cent. of the naphthylamine used can be obtained, but the method is not a convenient one on account of the large quantity of alcohol that has to be used.

ββ-Dinaphthyl crystallises in large colourless pearly plates, apparently rhombic, having a slight blue fluorescence. It dissolves easily in boiling benzene, xylene, and glacial acetic acid, and crystallises out very completely on cooling; in boiling alcohol, it is much less soluble, and only slightly so in chloroform and ether. It sublimes readily in little glistening leaflets, but is not volatile with steam. It melts sharply and constantly at 187·8° corr., or 183·5° uncorr. Its boiling point, determined with one of Bayly and Chorley's high temperature thermometers, was found to be 452° (uncorr.) under a pressure of 753 mm. Its composition, determined by a combustion, and its molecular weight, obtained from the depression of the freezing point of a benzene solution, agree very closely with those required for the formula $C_{20}H_{14}$.

0·2913 gave 1·0097 CO_2 and 0·1465 H_2O. C = 94·53; H = 5·60.
$C_{20}H_{14}$ requires C = 94·47; H = 5·52 per cent.

0·5985 gram of hydrocarbon dissolved in 105·5 grams of benzene lowered the freezing point by 0·11° C.
The formula $C_{20}H_{14}$ requires 254; found, 252.

Naphthyl-α-naphthaquinone, $C_{10}H_7{\cdot}C_{10}H_4O_2$[2 : 1 : 4].

To prepare this compound free from the diquinone, the hydrocarbon must be dissolved in a considerable excess of glacial acetic acid and the oxidation effected very rapidly. The following method of procedure has been found advantageous:—The hydrocarbon is dissolved in about 150 times its weight of boiling glacial acetic acid, three times its weight of chromic acid dissolved in boiling glacial acetic acid is added rapidly, and the whole boiled gently for 10 minutes; the hot solution is then poured immediately into a large quantity of cold distilled water. The quinone separates almost at once as yellow flocks, which, when collected and washed, have exactly the colour and appearance of precipitated mercuric oxide. It can be purified by crystallising it a few times from alcohol or ethylic acetate, the crystals being larger when the latter is used; by this treatment, the hydrocarbon is almost entirely converted into the quinone, only a very small quantity of phthalic acid being formed in addition.

Naphthylnaphthaquinone melts at 177° and crystallises in very small, orange-yellow needles, generally aggregated into rosettes. It dissolves readily in alcohol, ethylic acetate, and glacial acetic acid, forming clear orange-coloured solutions from which it crystallises well; it dissolves easily in benzene also, but does not crystallise well from this solvent. Its behaviour with sulphuric acid is characteristic; it dissolves readily in cold, concentrated sulphuric acid, giving a deep indigo-blue solution, from which water precipitates the quinone unchanged; on being heated, or on standing, the blue colour changes to purple, and finally to reddish-brown, when dilution no longer causes a precipitate. When heated with aqueous potash in presence of air, it dissolves, forming a deep, claret-coloured solution of the potassium compound of a quinol. When in solution, the quinone is sensitive to light, which should be excluded in working with it. If a clear yellow solution of the quinone be exposed to sunlight for some days, the colour slowly changes to a deep brownish-red, and a light chocolate amorphous deposit forms on the walls of the vessel. This deposit softens and runs together at about 205°, dissolves in concentrated sulphuric acid forming a deep green solution, and only appears to be partially dissolved by hot, aqueous potash. A sufficient quantity for a careful examination was not available.

A combustion (using lead chromate), and the depression of the freezing point of a benzene solution, prove that the quinone has the composition $C_{20}H_{12}O_2$, whilst its structure is shown by its behaviour on treatment with potash, and the products of its subsequent oxidation.

0·2073 gave 0·6455 CO_2 and 0·0828 H_2O. C = 84·92; H = 4·44.
$C_{20}H_{12}O_2$ requires C = 84·50; H = 4·23 per cent.

0·3448 gram of the quinone dissolved in 33·2 grams of benzene lowered the freezing point 0·185°.

Required for $C_{20}H_{12}O_2$ 284; found, 275.

Naphthylnaphthaquinol, $C_{10}H_7 \cdot C_{10}H_4(OH)_2$ [2 : 1 : 4].

On reduction, the quinone is converted into a colourless quinol; if the reduction is effected by zinc dust in a glacial acetic acid solution, the quinone is first reduced to the quinol and finally to the hydrocarbon itself. When an alcoholic solution is heated with a solution of stannous chloride, it is at once decolorised, and on filtering into water free from air, the quinol separates in colourless microscopic needles, which give a striated appearance to the shaken liquid. This compound melts at about 169—170°, and is reconverted into the quinone on oxidation. Oxidation only takes place slowly on exposing its solution to air, but is quickly effected by chromic acid. If dissolved in benzene and allowed to stand exposed to the air, greenish-brown needles are deposited, apparently of the quinhydrone. The quinhydrone appears to be produced also when the quinone is heated at 180—200° with an alcoholic solution of sulphur dioxide, the yellow solution changes to a greenish-brown, and blackish nodules are deposited on the sides of the tube. On evaporating the greenish-brown solution, a blackish residue is left which oxidises very slowly on exposure to air, but yields the quinone when dissolved in glacial acetic acid and oxidised by chromic acid.

Naphthylhydroxy-α-naphthaquinone, $OH\cdot C_{10}H_4O_2\cdot C_{10}H_7$ [3 : 1 : 4 : 2].

This compound is obtained when naphthyl-α-naphthaquinone is dissolved in a hot, dilute potash solution, and then treated with an acid. To prepare it, the quinone, in a finely divided condition, best obtained by dissolving it in glacial acetic acid and precipitating by water, is suspended in a 5 per cent. solution of potassium hydroxide and heated on a water bath; it slowly dissolves without any perceptible evolution of gas, forming a brownish-green liquid, the colour changing to a deep wine-red on standing in contact with air, or on shaking with it. The whole of the quinone never dissolves, a very small quantity of a black substance unacted on by the caustic potash always being left. On filtering, and slightly acidifying the deep crimson solution with hydrochloric acid, the naphthylhydroxynaphthaquinone is thrown down as brownish-red flocks very much resembling ferric hydroxide, though somewhat lighter and browner in colour. The compound separates from alcohol in small, nodular aggregates, almost black when moist, but forming a bright red powder when dry; under the microscope, this is seen to consist of minute, apparently crystalline, particles, but no distinct crystals can be recognised. Potassium hydroxide, added to an alcoholic solution of the quinone, instantly turns it a deep chromium green, changing to brown on heating, and finally to a deep claret colour on exposure to air.

Naphthylhydroxynaphthaquinone is a light red, crystalline powder, readily soluble in alcohol, benzene, glacial acetic acid, and ethylic acetate. It appears to melt at 186—187°, but the point of fusion is very difficult to determine, owing to the dark colour of the substance and to the fact that it sinters when near its melting point. It dissolves easily in cold, concentrated sulphuric acid, forming a reddish-brown solution, and also in solutions of the alkali or alkaline earth hydroxides, giving deep claret coloured liquids. It appears to form a compound with acid sodium sulphite. Its composition and molecular weight show that it is derived from naphthylnaphthaquinone by the substitution of a hydroxyl group for one of the hydrogen atoms in the quinone.

0·2022 gram gave 0·5904 CO_2 and 0·0746 H_2O. C = 79·63; H = 4·1.

$C_{10}H_7 \cdot C_{10}H_4(OH)O_2$ requires C = 79 99; H = 4·01 per cent.

The molecular weight was determined by Raoult's method in benzene; but, on account of the slight solubility of the compound, the observed depression was very small, and, consequently, the possible error large, but the result is sufficient to exclude any other interpretation of the analysis.

0·0765 gram of the compound dissolved in 25·2 grams of benzene lowered the freezing point by 0·055°.

Required for $C_{20}H_{12}O_3$, 300; found, 270.

Naphthylhydroxynapthaquinone can be reduced to a colourless compound, probably a naphthyltrihydroxynaphthalene. On shaking the crimson alkaline solution of the hydroxyquinone with sodium amalgam the colour slowly changes to greenish-yellow; but exposure to air instantly turns the solution deep crimson again. Hydrochloric acid, added to the yellow solution, precipitates a whitish, flocculent substance, not readily oxidised in the air, probably the trihydroxy-derivative; this dissolves readily in alcohol to a pale yellow solution, from which the substance crystallises, but enough has not been obtained to examine closely. A drop of a solution of potassium hydroxide added to this substance in presence of air instantly dissolves it, giving the crimson colour characteristic of the potassium compound of the hydroxyquinone.

If naphthylhydroxynaphthaquinone be dissolved in a very small quantity of aqueous ammonia, and any excess removed by heating, a deep red solution is obtained from which silver nitrate precipitates a purple flocculent compound containing about 40·44 per cent. of silver. It is unlikely that the precipitate would carry down and retain any very large quantity of the precipitant, and the result seems to indicate that an imide is produed on warming with the ammonia, and that a silver salt of this is actually obtained.

$C_{10}H_7 \cdot C_{10}H_4O(OAg)NAg$ requires Ag= 42·08. Found, 40·44 per cent.

This silver compound, on being heated, begins to decompose at about 180°, giving off a bright yellow substance, which solidifies to a very definitely crystalline mass on cooling. Only a very small quantity could be obtained. It dissolves easily in hot alcohol, glacial acetic acid, and ethylic acetate, and crystallises out remarkably well from all these solvents in long, slender needles. It melts at 225°, and appears not to be attacked on being heated with a 5 per cent. solution of potassium hydroxide.

Oxidation of Naphthylhydroxy-α-naphthaquinone by Potassium Permanganate.

A boiling alkaline solution of potassium permanganate readily oxidises the hydroxyquinone. It is dissolved in a dilute potash solution, heated or a water bath, and a solution of potassium permanganate added with continual stirring till the crimson colour just disappears. The liquid is then filtered from the oxide of manganese and extracted with ether; the yellow ethereal solution leaves a yellowish, viscid mass on distilling off the ether; and this, on being dissolved in the smallest possible quantity of boiling water, deposits white crystalline flocks on cooling. This substance is somewhat soluble in hot water, very slightly in cold, and readily in alcohol or ether. After three recrystallisations from hot water, it melts at 182—183°, and on distillation with soda-lime yields naphthalene. Sufficient was not obtained for analysis, but there seems no doubt that the substance obtained was β-naphthoic acid. The filtrate from the β-naphthoic acid, on evaporation, yields a small residue of phthalic acid.

ββ-Dinaphthadiquinone, $C_{10}H_5O_2 \cdot C_{10}H_5O_2$.

This quinone is produced when ββ-dinaphthyl, suspended in glacial acetic acid, is slowly oxidised by a considerable excess of chromic acid. It can be obtained in the following manner, though the yield is very small, not exceeding a tenth of the theoretical, and large quantities of other products are formed, the chief being a brown, friable mass, apparently consisting of β-naphthoic acid mixed with other substances of an acid nature, possibly quinonecarboxylic acids, and a small quantity of phthalic acid, amounting to about one-twentieth of the weight of ββ-dinaphthyl used. The hydrocarbon is suspended in about 50 times its weight of glacial acetic acid, and oxidised by five times its weight of chromic acid, also dissolved in glacial acetic acid and added in four portions, the solution being boiled for a few minutes after each addition, and allowed to cool and stand some hours before adding the next. To obtain the quinone, the liquid is poured into about four times its bulk of distilled water, when the quinone separates in light, yellowish-brown flocks. The dinaphthadiquinone can be easily separated from tarry matters and any naphthylnaphthaquinone that may remain, by repeated recrystallisation from alcohol, in which it is only very slightly soluble, whilst the other substances are very readily soluble.

$\beta\beta$-Dinaphthadiquinone is a light-brown, somewhat earthy looking powder, the particles having no definite crystalline shape. It separates from all solvents as crusts round the sides of the flask, or in brown nodules. It is moderately soluble in boiling glacial acetic acid and benzene, slightly in hot alcohol. It melts at about 216—217°, but its actual point of fusion is difficult to observe, as the substance darkens very much in colour at about 210°, and sinters between 212° and 213°. Dissolved in alcohol and boiled with a solution of stannous chloride, it appears to be reduced to a quinone. It dissolves readily in cold concentrated sulphuric acid giving a deep orange coloured liquid which changes rapidly to greenish-brown and finally to olive-green, and on being heated becomes reddish-brown. Water reprecipitates the quinone from the orange coloured solution, whilst the reddish-brown liquid obtained on heating remains clear on dilution. Light should be excluded in operations where the quinone is dissolved. When the brown solution of the quinone in alcohol is exposed to sunlight, its colour changes very rapidly to a brownish-red, while a dark solid, which appears not to be attacked by aqueous potassium hydroxide, is deposited. The quantity of quinone available was not sufficient to allow this action to be investigated. The dinaphthadiquinone dissolves on heating with aqueous potash yielding a deep claret coloured solution from which acids precipitate a dihydroxydinaphthadiquinone as chief product.

The composition of the substance agrees closely with that required by the formula $C_{20}H_{10}O_4$.

0·2225 gave 0·6233 CO_2 and 0·0687 H_2O. C = 76·4; H = 3·43.
$C_{20}H_{10}O_4$ requires C = 76·42; H = 3·19 per cent.

Dihydroxy-$\beta\beta$-dinaphthadiquinone, $C_{10}H_4O_2(OH)\cdot C_{10}H_4O_2(OH)$.

This compound is produced by an action exactly analogous to that yielding naphthylhydroxynaphthaquinone, that is, by dissolving the quinone in aqueous caustic potash and precipitating the hydroxy-derivative by an acid. The quinone is obtained in a finely divided condition by precipitating it from a glacial acetic acid solution by water; it is then heated on a water bath with a 5 per cent. solution of potassium hydroxide, when it slowly dissolves, forming a greenish-brown liquid which gradually changes to a deep claret colour as air obtains access. A small black residue always remains unattacked by the caustic potash; this may possibly be due to some action of light on the quinone during the process. On filtering and making slightly acid with hydrochloric acid, dihydroxydinaphthaquinone is thrown down as a bulky, very dark red, flocculent precipitate which is fractionally recrystallised from alcohol to free it from small quantities of tarry and more soluble substances formed at the same time. It separates from a hot alcoholic solution in red crusts, which, when dry, form a powder showing little trace ot crystalline form.

Dihydroxydinaphthadiquinone is a dark red, almost black, powder which gives a deep red streak on unglazed porcelain. It seems to melt at about 215°, but, owing to its dark colour the point of fusion cannot be accurately observed; it is easily soluble in glacial acetic acid, ethylic acetate, and alcohol. It dissolves easily in aqueous potash or soda giving deep, wine-red solutions, and also in concentrated sulphuric acid colouring it a deep reddish-brown.

Its composition shows that it has the formula $C_{20}H_{10}O_6$, being derived from the dinaphthadiquinone by the displacement of two hydrogen atoms by two hydroxyl groups, whilst its probable structure is indicated by the products of its oxidation.

0·1928 gave 0·4935 CO_2 and 0·0562 H_2O. C = 69·80; H = 3·24.
$C_{20}H_{10}O_6$ requires C = 69·35; H = 2·90 per cent.

Through the kindness of Mr. C. E. Groves, I have been enabled to compare this quinone directly with the diquinone of the same composition obtained by Stenhouse and Groves (*J. Chem. Soc.*, 1878, **33**, 415), from β-naphthaquinone, $C_{10}H_6O_2$ [1 : 2], by the action of somewhat dilute sulphuric acid and subsequent oxidation of the quinhydrone produced. Their dinaphthyl diquinone is of a bright orange colour, and resembles $\beta\beta$-dinaphtadiquinone in its sparing solubility in all ordinary solvents, but differs from it very markedly in all other points. It does not melt up to 300°, but darkens in colour and appears slightly to decompose. It dissolves easily in concentrated sulphuric acid, yielding a red solution, which is permanent at the ordinary temperature, but on heating the colour slowly changes, becoming successively green, bright blue, violet, and finally wine red. It dissolves in boiling alcoholic potash, giving a green solution, which on dilution with water and heating in the air changes to brown, and finally to pale yellow; the addition of an acid to the solution then throws down a yellow flocculent precipitate, very different in appearance from the dark red dihydroxy-$\beta\beta$-dinaphthadiquinone.

Oxidation of dihydroxydinaphthadiquinone.—In alkaline solution, it is readily oxidised if heated with a solution of potassium permanganate; phthalic acid, carbon dioxide, and a very small quantity of a curious red substance unattacked by potassium permanganate being the only products observed. To carry out the oxidation, the compound is dissolved in potash solution, heated to boiling and potassium permanganate added until the crimson colour of the dihydroxydinaphthadiquinone solution disappears; the filtrate is then acidified and extracted with ether. A considerable quantity of phthalic acid is formed, and in addition a very small quantity of a bright red solid, insoluble in water but readily soluble in ether, giving a bright red solution; the quantity obtained was not sufficient to ascertain its melting point. It dissolves in aqueous potash, giving a brown solution which is not changed by boiling with potassium permanganate. On adding hydrochloric acid to the brown liquid, the compound is reprecipitated in bright carmine-red flocks.

The author is engaged in investigating the sulphonic acids of $\beta\beta$-dinaphthyl and on the synthesis of $\alpha\beta$-dinaphthyl, and hopes to communicate the results to the Society.

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LXXII.—*A Comparison of some Properties of Acetic acid and its Chloro- and Bromo-derivatives.*

By Spencer Umfreville Pickering, F.R.S.

In a recent communication to this Society (Trans., 1894, **65**, 402) Dr. Perkin alluded to the differences in the thermal behaviour of acetic acid and its chloro-derivatives when dissolved in water, the heat evolved increasing rapidly with the extent to which chlorine is substituted for the hydrogen.* The observations, however, on which this statement was based were only of a rough character, and it appeared desirable that more exact measurements of the heat of dissolution should be made.

Since the mono- and trichloracetic acids are solid at ordinary temperatures, their heat of dissolution in the liquid condition—in which condition alone the results would be satisfactorily comparable with each other—must be deduced from their heat of dissolution as solids by means of the heat of fusion; it was necessary, therefore, to determine the latter, and, as the heat of fusion at temperatures other than that of normal fusion was required, it was necessary also to determine the heat capacity both in the solid and in the liquid conditions. These three properties were measured in the case of all four acids, so as to afford further information respecting the whole series.

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* It is not quite correct, however, that liquid acetic acid dissolves with absorption of heat: the heat disturbance at all ordinary temperatures is a small positive quantity.

Series of freezing-point determinations were also made in the case of all the acids.

With the brominated acids, the determinations were confined to the heat of dissolution in the solid condition.

Heat Capacity and Heat of Fusion.

The heat capacity and heat of fusion were determined in the same manner as that described in the *Proc. Roy. Soc.*, 1890, **49**, 15, the substance being heated to the required temperature in a platinum bottle and then plunged into the calorimeter. A single experiment will suffice for the determination of the heat capacity in the case where the cooling (or heating) is accompanied by no change of condition; but if a change, such as solidification, occurs, two determinations, starting with the contents of the bottle at different temperatures, are necessary, the difference between the heat evolved giving the heat capacity of the liquid between the two initial temperatures. Having determined this, and also the heat capacity in the solid condition, the heat of fusion may be deduced from one or other of the determinations.

The average mean error in the present determinations is 3·7 per cent. of the values obtained: it is higher than usual in such cases, owing to there being one exceptional value (with liquid chloracetic acid), the omission of which would reduce the error to nearly half this quantity.

The experimental details are given in Table I, and the final results in Table II (pp. 676—677). If t and t' are the initial and final temperatures of the calorimeter, T the initial temperature of the bottle, W the water equivalent of the calorimeter and its contents, w' that of the bottle and the thermometer in it, and w the weight of substance in the bottle, the heat capacity per gram of substance is, in a case where no change of state has occurred, $\frac{(t'-t)\,W-(\tau-t')w'}{(\tau-t)w}$, or in a case where a change of state has occurred it is $\left[\frac{(t'-t)\,W-(\tau-t')w'}{w} - \frac{(t'_1-t_1)W_1-(t_1-t'_1)w'_1}{w_1}\right] \div (\tau-\tau_1)$. In all cases, duplicate determinations, at as nearly as possible the same temperature, were made.

Although it does not seem to be generally known, it has been well established that solid chloracetic acid exists in two modifications, one having a freezing-point of 61·18° (according to my own determinations) the other one of 56·01°. This fact was first noticed by Tollens (*Ber.*, 1884, **17**, 665), and the heat of conversion of the one into the other has been measured by Tanatar, who determined the heat of dissolution of each form (*J. Russ. Chem. Soc.*, 1892, **24**, 694). There are yet other modifications as will be stated below. The molten acid generally crystallises at 56·01° in the β-form, but on partially melting any acid which has been kept for some length of time its freezing-point, from causes to be mentioned shortly, will be found to be that of the α-form, 61·18°. The existence of these modifications introduces some uncertainty into the determinations with the acid, especially as, although the platinum bottle contains a thermometer, this cannot be stirred in it during the cooling, and hence the temperature at which solidification is occurring cannot be ascertained accurately. On working out the results (expts. 7, 8, 9, 12, and 13) it was found that in one of the three determinations with an initial temperature of 75—76°, namely, in expt. 12, a notably smaller evolution of heat had occurred than in the other two, and that, similarly, in one of the two determinations with an initial temperature of 56—57°,* namely, in expt. 13, that the heat evolved was considerably less than in the other. It was assumed that in those cases where more heat had been evolved, that the α-form had crystallised at 61·18°, and that in the others the β-form, crystallising at 56·01°, had separated, Tanatar's determinations having shown that the heat of formation of the former is greater than that of the latter. The correctness of this supposition was proved by the fact that the three determinations in which the larger heat of evolution was observed (7, 8, and 9) when combined together, led to the same value for the heat capacity of the liquid acid as did the two determinations with the smaller evolution (12 and 13; see Table II). This, however, it must be remarked, simply proves that the two sets of determinations are concordant in themselves, and that the greater evolution of heat in certain cases is not due to error; it does not prove that the freezing-points taken in the calculations are necessarily correct, for, the heat capacity of the liquid being deduced from the difference between two determinations, the results will not be appreciably affected if any alteration is made in the freezing-point in the two cases; in the same way, the results obtained are practically independent of the value taken for the heat capacity of the solid acid, and this need not be the same in the case of both forms of the acid, as was assumed in the calculations.

The heat of fusion deduced for the α-form is 3895 cal. at 61·18°, and for the β-form it is 3330 cal. at 56·01°: reducing the former to the same temperature as the latter—56·01°—it becomes 3868 cal., and hence the conversion of the β- into the α-form evolves 538 cal. Tanatar's heat of dissolution determinations lead to 700 cal. as the value of this change, a sufficiently close concordance, considering that different methods were employed, and that his value applies to the temperature of 20° instead of 56·01°.

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* The acid was in a liquid condition at these temperatures, although below the normal melting point of the α-form.

One determination (14) of the heat capacity of the solid monochloracetic acid gave a very different value from the other two; it is possible that in this case the acid was in the β-form; but in the absence of any confirmatory evidence it would not be safe to draw any such conclusions.

The freezing-point of dichloracetic acid was found to be 10·8°; the only statement heretofore existing respecting it being that it solidifies below 0°.

It was found that acetic acid took too long a time in fusing or solidifying when in the bottle in the calorimeter to permit of its heat of fusion being accurately determined in that manner. It was determined, therefore, by measuring its heat of dissolution at 13·6°, both in the liquid and solid condition (Table III). These results give 2626 cal. as the heat of fusion at this temperature. This value is in fair agreement with Petterson's value of 2660 cal. at 3° to 5·5° obtained by direct determination (*K. Gesellschaft. der Wissenschaften zu Upsala*, May, 1879, 36), and with Berthelot's, obtained in the same manner as that here described, of 2530 cal. at 7° (*Compt. rend.*, 1873, **77**, 26). Reduced to a temperature of 16·9°, by means of the heat capacities given in Table II, these determinations give

Berthelot	2642	cal.	at 16·9°.
Petterson	2779	„	„
Pickering	2657	„	„

Petterson also determined the heat capacity of the liquid acid (*J. pr Chem.*, 1881, [2], **24**, 293). The value which he found, 28·74 from 0 to 47°, and 29·82 from 0° to 100°, differed so much from my own that it was thought advisable to make a fresh determination with an entirely different sample of acid. This other sample, however, gave identical results: 32·556, as against 32·694 with the first sample; and so also with the solid acid, 23·352 was obtained with the second sample of acid, 23·130 with the first (Table III, p. 678): there is, therefore, no ground for discrediting the present values. The differences between the heat capacities in the liquid and solid conditions, $C-c$ in the table, gives the rate at which the heat of fusion varies with the temperature; if $C-c$ is positive the heat of fusion increases with the temperature, and *vice versâ*.

Heat of Dissolution.

The results are given in Table III, the values being deduced by means of the equation $(t'-t)\mathrm{WM}/w$, in which M represents the molecular weight, and the other letters have the same signification as before. The values for acetic acid at 18·5° have already been given in the *Phil Mag.*, 1892, **34**, 35: they apply to a temperature 3° higher than the others.

To obtain the values for infinite dilution, the acid taken was added to the calorimetric water in three successive portions, and the heat of dissolution at three different strengths was thus obtained. On plotting out the values against the weight of substances taken, the figure can be extended with a fair degree of certainty to the zero point (infinite dilution), and, although extrapolation is always objectionable, the values thus obtained are more correct for purposes of comparison than those which apply to some arbitrarily selected state of dilution. The three weights given under w for each substance represent the total amounts added after the one, two and three additions respectively, and, similarly, $t'-t$ represents the total rise of temperature above the first initial temperature. The heat capacity of the liquid in the calorimeter was taken to be equivalent to that of the water (600 grams) + the acid added when regarded as liquid.

In the case of acetic acid and dichloracetic acid. it will be seen that the values increase somewhat rapidly with the dilution, and indicate a value at infinite dilution greater than any obtained in the actual determinations: with mono- and tri-chloracetic acids, on the other hand, constancy appears to have been reached in the determinations, in the former case at a dilution of $200H_2O$ or less, in the latter at a dilution of about $500H_2O$

The values for the heat of dissolution of liquid acetic acid show an increase with fall of temperature; this is the reverse of what generally occurs with a substance evolving heat on dissolution. Determinations have been made by Berthelot (*loc. cit*) which lead to the same conclusion, and which, moreover, are in good agreement with the present determinations. With 1 gram-molecular proportion of the acid in $200H_2O$, we get—

	At 23·0°	240 cal.	Berthelot,
	,, 18·5	275 ,, ...	Pickering,
	,, 13·6	367 ,, ...	Pickering,
	,, 7·0	400 ,, ...	Berthelot,
whence	,, 15·5	315 ,, ...	Berthelot,
		330 ,, ...	Pickering.

The heat of dissolution of the three bromacetic acids was determined in the solid condition. The values, however, with the dibrom-acid are of doubtful accuracy. Its extremely hygroscopic nature rendered it impossible to dry it even over phosphoric anhydride in a vacuum, and the amount of material available was not sufficient to permit of very satisfactory fractionation by distillation under reduced pressure.

Dr. Perkin, who was good enough to perform this fractionation, obtained three fractions with the following boiling- and freezing-points.

Boiling-point.	Freezing-point.
194·0—195·5°	30·6°
195·5—197·0	36·0
197·0—199·0	37·8

These were used in the three determinations given in Table III, but it is probable that even the last sample was not quite anhydrous, as its freezing-point is not so high as that given by Hofmann (53°). There was also not sufficient of the sample to admit of determinations with different quantities of water, so that the value for infinite dilution could not be estimated. It is probable that with a perfectly anhydrous acid, the heat of dissolution in infinity of water would be a very small negative quantity.

Freezing-points.

These were determined in order to ascertain whether any of the acids formed crystalline hydrates. No such hydrates were isolated, but the results proved to be of considerable interest in other respects. They are given in Tables IV and V, and in Figs. I, II and III. Those with acetic acid have already been published in the Transactions, (1893, **63**, 1018, 1026).

In the case of monochloracetic acid, we have the two modifications previously mentioned, the α with a freezing-point of 61·18°, and the β with a freezing-point of 56·01°, and these two modifications can be obtained, not only from the liquid acid, but also from its solutions, so that we get two distinct freezing-point curves, one uniformly lower than the other, according to which of the two modifications crystallises. For the second series of determinations given in Table IV (p. 679), the two freezing-points were obtained from each different strength of solutions used; by allowing the liquid to cool and crystallise spontaneously, the β-modification was invariably obtained (in this series), while the introduction of a trace of the α-modification—some of the solid acid which had been kept for some time—caused the crystals to change into the α-form, the temperature rising immediately, and giving the freezing-point of the latter modification. The freezing-points of the α-modification in this series are marked by crosses in Fig. I, and those of the β by dots enclosed in circles. It will be seen that the two curves are nearly parallel throughout, there being a fairly constant difference of 4° to 6° between them.

On drawing Dr. Perkin's attention to the existence of these two freezing-points, he was kind enough to verify my observations in the case of the anhydrous acid, and he also made the observation that there possibly existed a third modification. He said: "If the acid be melted in a test-tube and then immersed in cold water nearly to the top of the fused acid, so that its walls are covered with a crystalline coating, the crystals continue to slowly grow, the thermometer being as low as 45—46°. If now a crystal of the 61° freezing-point acid be added to the surface it immediately becomes opaque, and in a few seconds the whole is solid, the thermometer rising above 61°." As I failed to verify this observation of a freezing-point of 45—46° with the sample of acid then in my possession, I attributed (as also Dr. Perkin did subsequently) the low temperature observed to a supercooling of the thermometer, owing to its having been held stationary in the liquid; but on working out the results of a previous series of freezing-points made with another sample of acid, it appeared that Dr. Perkin's observation was correct, and that a third modification existed in reality. This series (Series I in Table IV) is shown in Fig. I by simple dots. The first two observations, it will be seen, evidently refer to the crystallisation of the β-modification; there is then one anomalous point at 96 per cent., followed by four others which lie on a perfectly regular curve, parallel to, but considerably lower than the curve of the α- and β-modifications. On producing this curve back to the origin, we get 42·7° indicated as the freezing-point of the corresponding acid, a temperature which agrees very well with Dr. Perkin's observations.

It, moreover, appeared to me that the anomalous point at 96 per cent. above mentioned could scarcely be attributed to any experimental error, and in the presence of the fact that three modifications were already known, it did not seem unreasonable to conjecture that this point might refer to the crystallisation of a fourth. On drawing a line through it, parallel to the other curves, the freezing-point of this supposed fourth modification would probably be about 50°. It occurred to me then that on first determining the freezing point of chloracetic acid (the same sample as that used in Series I), I had obtained certain anomalous results, which, being at the time inexplicable, I had discarded as erroneous. The observations—each of them an independent one—were as follows.

Freezing-point........	43·65°	43·75°
,, ...	43·85	
,, ...	50·05	50·05
,, ...	50·05	
,, ...	55·90	55·90
,, ...	55·70	
, ...	56·10	

The last three of these evidently refer to the β-modification (f. p. 56·01°), and the first two to the δ-modification subsequently obtained by Dr. Perkin, whilst the intermediate ones agree perfectly with the indication afforded by the freezing-point at 96 per cent. in Series I. There can be little doubt, therefore, but that we have as many as four distinct crystalline modifications of chloracetic acid.

		Difference.
α-freezing-point......	61·18°	5·17°
β- „	56·01	
γ- „	50·05	5·96
δ- „	43·75	6·30

The differences between their freezing-points show a gradual increase as we descend in the series, but are not far from being constant throughout. The α, which is evidently the most stable form, crystallises in transparent prisms, the β in tables, and the δ in laminæ. The appearance of the γ-form was not specially noticed.

Attempts were then made to ascertain the circumstances under which these various modifications separated from the liquid acid. It was found in this case, as in that of the hydrates of soda (Trans., 1893, **63**, 890), that slow cooling without agitating the liquid is most favourable to the crystallisation of the substance with the lowest freezing-point, whereas rapid or excessive cooling, or agitation, ensures the crystallisation of the substance with the higher freezing-point. In the case of chloracetic acid, gentle and careful cooling produces the crystallisation of the γ-modification, melting at 50·05°; and on cooling this further, as by plunging the containing vessel into cold water, or on rubbing the inside of the vessel with the thermometer, it becomes opaque and converted into the β-modification melting at 56·01°. If a solution, instead of a pure acid, is taken, the existence of the γ-modification becomes more transitory, and more and more so as the amount of water added is greater. To obtain the α-modification, melting at 61·18°, excessive cooling, such as placing the containing tube in liquid nitrous oxide, was found to be necessary, and this method was always effectual; it was also found that the α-form was produced by the rapid condensation of the vapour of the acid, and hence, on keeping some of the acid in a bottle it becomes converted into this form, although the change is not brought about directly by the lapse of time, as was proved by keeping the acid in a vessel which it completely filled, and where condensation of vapour was prevented.

Any modification in the treatment of the liquid, prior to allowing it to crystallise, appeared to have no influence on the nature of the crystallisation, and these three modifications were obtained in the manner described with absolute certainty as often as was desired.

The samples of acid (two in number) used in the latter experiments were different from those used for the freezing-point determinations, and from them it was found impossible to obtain the γ-modification. In view of the previous results, confirmed by Dr. Perkin's observation, and the fact that a whole series of freezing-points of this modification had been obtained, it is impossible to doubt its existence, and we can only conclude that some condition of purity or impurity is necessary for its formation. Unfortunately the sample of acid from which it had been obtained was used up before the existence of these various modifications had been realised.

Similar methods were adopted in examining the other chlorinated derivatives of acetic acid, and also acetic acid itself and its bromoderivatives, to see if any of them formed other modifications, but without success in any case.

The results with the acids at present under examination were in no case sufficiently numerous to satisfactorily prove any changes of curvature which may exist, but it is impossible not to be struck by the fact that there seems to be a very marked change of curvature in the case of trichloracetic acid at a composition represented by an equal number of molecules of the acid and of water (Fig. III).

In the case of the weaker solutions, mono- and dichloracetic acids both suggest a change at the same point, namely, 5 or 6 mols. of water to one of acid (17 and 16 mols. of acid to $100H_2O$), while with the trichlor-acid the results appear to be more complicated.

Comparison of the Properties.

Table VI gives a comparative view of the properties here examined, together with three others previously known.

The first step in the chlorination of acetic acid might be reasonably expected to produce a greater alteration in the properties of the acid than subsequent steps do, acetic acid thus appearing to be the exceptional member of the series; this, as is well known, is conspicuously so in the case of the boiling-points, where the introduction of the first atom of chlorine produces a rise of 71°, and the other two a rise of only 5° and 2° respectively. A similarly exceptional position is assigned to acetic acid by some of the other properties, but not by all of them. The heat capacity in the liquid condition does so especially, the values for the three chlorinated acids lying on a straight line (differences equal), whereas acetic acid lies considerably off this line. The sp. gr. and the heat of dissolution in the liquid condition show a similar behaviour, though in a less marked manner, the differences between the mono- and dichlorinated acids being rather larger than those between the di- and the trichlorinated acids, though in both cases these differences are approximately equal as compared with the difference between acetic acid and its monochlorinated derivative. These properties it will be noticed all refer to the substances in the liquid condition, and we might have expected the magnetic rotations to behave similarly, since they also apply to the liquids; but the values do not appear to me to justify such a conclusion, and, taken as they stand, they would seem to indicate that acetic acid and its di-derivative are analogous, while the mono- and trichlorinated derivatives are also analogous, the difference between the values for the first pair being 2·768 and between the second pair 2·570; a similar arrangement into pairs is noticeable in the case of the freezing-points. where we have 17° and 11° on the one hand, and 61° and 59° on the other; and the same has already been noticed in the heat of dilution, where we get the heat evolved extending to great dilutions in the case of acetic acid and dichloracetic acid, but becoming soon constant in the case of the mono- and trichlor-acids. We have, therefore, four properties assigning an exceptional position to acetic acid, and three properties indicating a close relationship between the alternate members of the series.

The properties given in the third portion of Table VI (p. 682) deal with the acids in the solid condition. The heat capacity of the solids, especially when we consider the values per unit weight, indicate an exceptional position for acetic acid, whereas the heat of fusion, reduced to a temperature of 15·5°, indicates no simple relationship at all between the acids. The heat of fusion of the monochlor-acid is evidently exceptionally high for its place in the series, but that may be due to its existence in several different forms, and it is to the one with the largest heat of fusion that the numbers quoted refer; one of those with a smaller heat of fusion would evidently fit into the series better, and it is, therefore, probable that it is one of those--probably the γ- or δ-acid—which is comparable in the solid state with the other members of this series.

The difference between the heat capacities of the acids in the two conditions ($C - c$) is also given in the table, and is worthy of attention, inasmuch as it is the only property which indicates a simple relationship between all the members of the series. The differences between the consecutive values give numbers which lie on a straight line well within the limits of experimental error, and hence the values themselves form a parabola of the simplest order. Too much stress, however, must not be laid on this point, owing to a peculiarity in some of the values for $C - c$. In two cases they are negative, and, being such, it is doubtful how far they represent the true facts of the case. The heat capacity of the solid being greater than that of the liquid ($C - c$ negative) means that the heat of fusion increases with fall of temperature, and that there will be no temperature, however low, at which crystallisation is impossible (see *Proc. Roy. Soc.*, **49**, 11). Such an exceptional behaviour has been attributed in the few cases where it has been noticed to the apparent value for the heat capacity of the solid being abnormally high, owing to its including part of the heat of fusion, the fusion in such a case being of a gradual nature, extending over an appreciable range of temperature. Such an explanation, however, can hardly hold good in the present cases of the di- and trichloracetic acids, since their heat capacity was determined at temperatures considerably below their freezing-points. Another possible explanation, however, is that the heat capacities vary considerably with temperature, and that as the determinations with the solids and liquids were not made at the same temperature they are not strictly comparable. This would obviate the difficulty that there seems to be in understanding the meaning of a negative value for $C - c$, but, on the other hand, if we adopt it, we must conclude that the simple relationship shown by the series at present under examination is accidental. The subject certainly deserves further investigation.

The molecular depression of the freezing-point of water by the acids, and of those of the acids by water, each at two different strengths, is given in the table. The values, however, it must be remembered, have no pretensions to much accuracy. The depression of the freezing-point of water by the acids is approximately normal, except in the case of the trichlorinated acid, where it is exceptionally high, and in every case it decreases considerably with an increase in the water added. A similar decrease is observed in the molecular depression of the freezing-points of the acids by water. The values obtained for weak solutions do not agree well with those calculated according to van't Hoff's formula (given in the table), but it is probable that they would do so better if still weaker solutions had been investigated. This at any rate is the case with acetic acid, where such solutions have been examined. It is only in the case of the trichlorinated acid that such an agreement would seem to be impossible.

It will be noticed, especially on examining Fig. 2, that the depression of the freezing-point of water by all the acids is represented by a wavy curve, except perhaps in the case of acetic acid, and that this waviness becomes more pronounced the higher the degree of chlorination.

Table VII gives the values for the heat of dissolution of the solid bromacetic acids, and, for the sake of comparison, those of the solid chloracetic acids. The latter, of course, will exhibit the peculiarity noticed in the heat of fusion, chloracetic acid giving an exceptionally large (negative) value, and it is a point of special interest to note that bromacetic acid appears to hold a precisely similar exceptional position in its series; indeed all the differences between the values for the brominated acids are strikingly analogous to those between the values for the chlorinated acids, although they are all appreciably smaller. This would lead us to the inference that bromacetic acid also exists in several modifications, the one here examined being that corresponding to the α-chloracetic acid, yet, as has been mentioned, all attempts to prepare other modifications of bromacetic acid failed.

TABLE I.—*Determination of the Heat Capacity and Heat of Fusion.*

Water equivalent of bottle, &c. = 2·43 grams = w'.
” ” calorimeter, &c. = 606·56 grams = W.

Substance.	Freezing point.	Weight taken, w.	τ.	t'.	$t' - t$.
1. Acetic acid..........	16·91°	32·80	61·54	16·15	1 510°
2. ”	”	”	62·00	16·20	1·542
27. ”	”	31·53	69·21	13·65	1·765
28. ”	”	”	69·49	14·52	1·777
5. ”	”	30·47	−16·21	12·83	0·668
6. ”	”	”	−13·74	12·62	0·626
29. ”	”	34·52	−16·07	12·00	0·728
30. ”	”	”	−14·98	11·98	0·712
7. Monochloracetic acid	61·18	42·54	75·83	19·33	4·747
8. ”	”	”	75·41	19·53	4·606
9. ”	”	”	57·14*	18·62	3·983
10. ”	”	”	41·50	15·88	0·815
11. ”	”	”	45·54	14·88	0·905
12. ”	56·01	”	76·05	18·63	4·281
13. ”	”	”	55·88*	17·65	3·598
14. ”	?	”	45·27	15·43	0·967
15. Dichloracetic acid....	10·80	41·48	50·16	18·18	0·961
16. ”	”	”	50·40	18·77	0·960
17. ”	”	”	3·76	16·19	1·357
18. ”	”	”	3·16	16·50	1·380
19. ”	”	”	−19·03	14·55	2·027
20. ”	”	”	−20·36	15·57	2·122
21. Trichloracetic acid...	59·10	49·05	82·13	17·55	3·174
22. ”	”	”	83·17	17·28	3·202
23. ”	”	”	61·30	17·29	2·502
24. ”	”	”	61·08	17·00	2·485
25. ”	”	”	47·11	15·53	1·259
26. ”	”	”	47·43	15·88	1·318

* Liquid (superfused) at commencement of the determination.

TABLE II.—*Heat Capacity and Heat of Fusion Results.*

Experiment.	Substance.	Property.	Per gram.			Per gram-molecule.		Mol. weight.	Temp.
1 2	Acetic acid	Heat capacity, liquid	0·5418 0·5486	0·5449	0·5438	32·604	32·628	60	62—16°
27 28	”	”	0·5341 0·5512	0·5426		32·556		”	69—14
5 6	”	Heat capacity, solid	0·3779 0·3931	0·3855	0·3879	23·130	23·241	”	−15—13
29 30	”	”	0·3852 0·3933	0·3892		23·352		”	−16—12
	”	Heat of fusion*	44·28			26·57		”	16·91
	”	C − c		0·1559		9·387		—	—
7 and 9 8 and 9 12 and 13	Monochloracetic acid	Heat capacity, liquid	0·4428 0·3952 0·4132	0·4271		40·361		94·5	76—56
10 11	”	Heat capacity, solid	0·3641 0·3635	0·3638		34·379		”	45—15
11 14	”	”	(0·4050?)			—		”	45—15
9	—	Heat of fusion, α	41·217†			3895·0†		”	61·18
13	”	” β	35·237‡			3330·3‡		”	56·01
	”	C − c	0·0683			5·982		—	—

* From the heat of dissolution determinations at 13·6°, Table III. These give the heat of fusion at 13·6° to be 2626 cal.

† These values give the heat of fusion at the normal melting point. At the initial temperature of the determination (57·14°), they are 40·961 and 38·969 respectively.

‡ At the initial temperature of the determination (55·88°), these numbers are 35·229 and 3329·6 respectively.

TABLE II—*continued.*

Experiment.	Substance.	Property.	Per gram.		Per gram molecule.	Mol. weight.	Temp
15 16	Dichloracetic acid	Heat capacity, liquid	0·3806 0·3854	0·3830	49·407	120	50—18°
17 and 19 18 and 20	,,	Heat capacity, solid	0·4019 0·4105	0·4062	52·400	,,	−20—3
17 18	,,	Heat of fusion	14·216 14·119	14·168	1827·6	,,	10·80
	,,	$C - c$		−0·0232	−2·993	,,	—
21 and 23 22 and 24	Trichloracetic acid	Heat capacity, liquid	0·3561 0·3586	0·3574	58·435	163·5	83—61
25 26	,,	Heat capacity, solid	0·4520 0·4669	0 4595	75·128	,,	47—16
23 24	,,	Heat of fusion	8·766 8·499	8·628	1410 7	,,	59·10
	,,	$C - c$		−0·1021	−16·693	,,	—

TABLE III.—*Heat of Dissolution Results.*

Substance.	Weight taken, *w*.	Solvent.	Water equiv. of solvent and apparatus, W.	*t*.	*t'* − *t*.	Mol. heat of dissolution	
CH_3·COOH, liquid	4·571	$411H_2O$	565·15	18·5	0·044°	328	
„	9·105	$207H_2O$	567·23	„	0·081	275	
„	13·619	$139H_2O$	569·30	„	0·116	268	
„	—	∝ H_2O	—	„	—	455	
„	10·13	$197H_2O$	611·83	13·60	0·1007	365	367
„	10·16	$198H_2O$	611·81	„	0·1015	370	
CH_3·COOH, solid	10·08	$198H_2O$	611·78	13·60	−0·6251	−2276	−2259
„	9·36	$214H_2O$	611·43	„	−0·5723	−2242	
CH_2Cl·COOH, solid........	3·621	$870H_2O$	607·45	15·54	−0·211	−3351	−3352
„	7·965	$396H_2O$	609·03	„	−0·463	−3347	
„	15·981	$197H_2O$	611·95	„	−0·928	−3357	
„	—	∝ H_2O	—	„	—		−3352
CH_2Cl·COOH, liquid.......	—	∝ H_2O	—	„	—		+270
$CHCl_2$·COOH, liquid.......	5·539	$776H_2O$	608·25	15·88	0·196	2770	
„	10·817	$398H_2O$	610·27	„	0·355	2584	
„	21·922	$196H_2O$	614·52	„	0·637	2303	
„	—	∝ H_2O	—	„	—	2930	
CCl_3·COOH, solid	5·820	$936H_2O$	608·23	15·31	0·158	2697	2702
„	10·963	$498H_2O$	610·08	„	0·298	2706	
„	22·210	$245H_2O$	614·13	„	0·553	2505	
„	—	∝ H_2O	—	„	—		2702
CCl_3·COOH, liquid.......	—	∝ H_2O	—	„	—		5277
CH_2Br·COOH, solid........	6·527	$712H_2O$	608·93	15·45	−0·242	−3143	
„	12·679	$365H_2O$	611·60	„	−0·479	−3213	
„	23·321	$199H_2O$	616·18	„	−0·901	−3308	
„	—	∝ H_2O	—	„	—	−3063	
$CHBr_2$·COOH, solid........	19·958*	$364H_2O$	616·11	15·32	−0·042	− 281	
„	15·167†	$479H_2O$	613·70	15·27	−0·102	− 899	
„	10·211‡	$712H_2O$	611·23	15·28	−0·063	− 818	
$CHBr_3$·COOH, solid	12·390	$799H_2O$	612·32	15·16	0·014	626	
„	23·762	$417H_2O$	618·00	„	0·062	475	
„	48·075	$206H_2O$	630·15	„	0·065	251	
„	—	∝ H_2O	—	„	—	840	

* Sample III. † Sample II. ‡ Sample I.

TABLE IV.—*Freezing-points of Solution of Monochloracetic acid.*

Per cent. $CH_2Cl·COOH$.	Mols. H_2O to $CH_2Cl·COOH$.	Freezing-point.	Depression.
First Series. Chloracetic acid, β, γ or δ, crystallises.			
100	0	56·01 β	0
97·51	13·43	51·4 β	4·61
96·02	21·80	41·4 γ	8·65
93·96	33·75	29·8 δ	13·95
87·07	73·84	16·8 δ	26·95
80·36	128·3	3·1 δ	40·65
73·38	190·4	−9·4 δ	52·85
Water crystallises.			
	Mols. $CH_2Cl·COOH$ to H_2O.		
65·37	35·96	−15·9	—
56·38	24·51	−11·1	—
47·10	16·96	− 8·25	—
29·87	8·11	− 4·95	—
16·11	3·66	− 2·75	—
8·45	1·76	− 1·60	—

Per cent $CH_2Cl·COOH$.	Mols H_2O to $CH_2Cl·COOH$.	Freezing-point.	Depression.
Second Series. Chloracetic acid, α or β, crystallises.			
100	0	61·18α	0α
96·19	20·18	52·13α 47·74β	9·05α 8·27β
92·41	43·13	44·32α 38·63β	16·86α 17·38β
88·69	66·94	35·94α 31·39β	25·24α 24·62β
84·95	92·99	28·34α	32·84α
81·46	119·5	20·12α 15·88β	41·0α 40·13β
76·52	161·1	11·22α 5·48β	49·96α 50·53β
71·00	214·4	− 0·40α − 3·70β	61·58α 59·71β
65·59	275·4	− 7·8α	68·98α
60·83	339·7	−13·5α	74·68α
Water crystallises.			
	Mols. $CHCl_2·COOH$ to H_2O.		
55·66	23·91	−11·9	—

TA

TABLE VI—*continued.*

Per cent. $CHCl_2 \cdot COOH$.	Mols. H_2O to $CHCl_2 \cdot COOH$.	s.	Dichl Heat of capacity of solid. Per gram-mol.		Heat of fusion at 15·5°. Per gram.		Heat of fusion at 15·5°. Per gram-mol.		Difference between heat capacity per gram, C − *c*.	
			23·241		41·28		2625		0·1559	
Dichloracetic acid		241		11 138		3·04		−996		0·0926
			34·379		11·24		3621		0·0633	
100	0	424		18·021		27·07		1807		0·0865
96·86	28·23		52·400		14·17		1814		−0·0232	
Diff.	20	−0·0533		12·728		5·54		−325		0·0789
Trichloracetic	0·4595		75·128		8·63		2139		−0·1021	

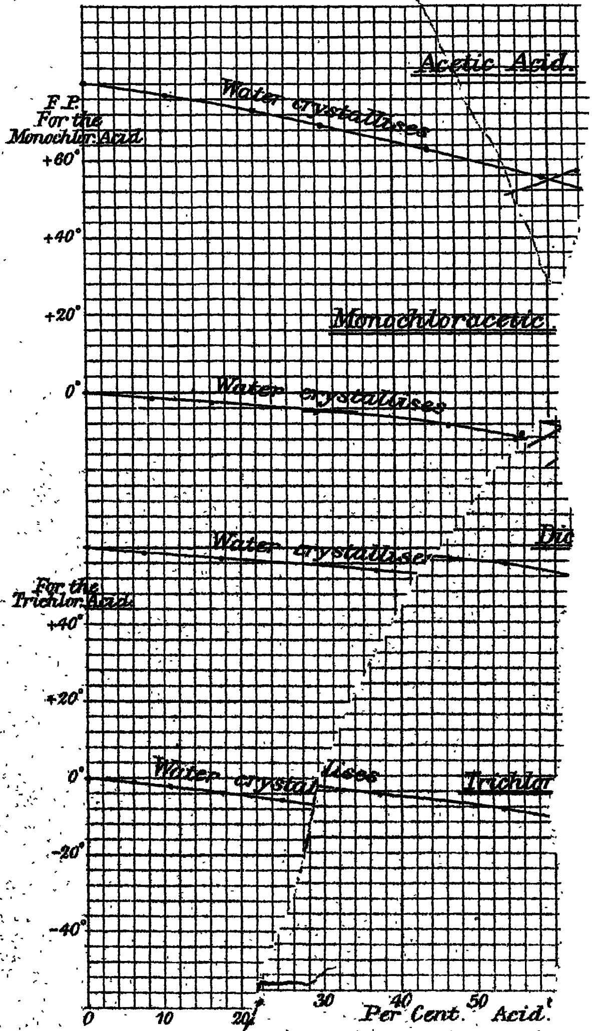
Acid.	Mol. depression of the freezing-point of water by the acid.		Mol. depression of the freezing-point of the acid by water.		
	At 1 mol. to $100H_2O$.	At 40 mols. to $100H_2O$.	At 10 mols. to 100 mols. acid		At 200 mols. to 100 mols. acid.
Acetic	1·08°	0·56°	0·45°*	Theory = 0·63°	0·21
α-Chloracetic	0 91	0·45	0·45	„ = 0·57	0·29
Dichloracetic	0·88	0·63	0·52	„ = 0·88	—
Trichloracetic	1·50	0·98	0·52	„ = 1·56	0·51

* At 1·6 mols. the molecular depression is 0 6°.

S.U. PICKERING.

FIG. I.

FREEZING-POINTS OF SOLUTIONS OF ACETIC
PLOTTED AGAINST PERCENTAGE



NOTE.—With Monochloracetic Acid, • refers to
⊙, to the second series, ×, to the secon
was touched off with the α modification

TABLE VII.—*Heat of Dissolution per Gram-Molecule of the Solid Acids at about* 15° *in* ∝ H_2O.

Acid.	Heat of dissolution.		Acid.	Heat of dissolution.	
Acetic..........	−2223		Acetic.........	−2223	
Diff...		−1129	Diff...		−840
Chloracetic......	−3352		Bromacetic.....	−3063	
Diff...		4468	Diff...		2782
Dichloracetic....	1116		Dibromacetic.....	(−281)	
Diff...		1586	Diff...		1121
Trichloracetic....	2702		Tribromacetic...	840	

FIG. 2.—Depression of the Freezing-point of Water by the Acids.

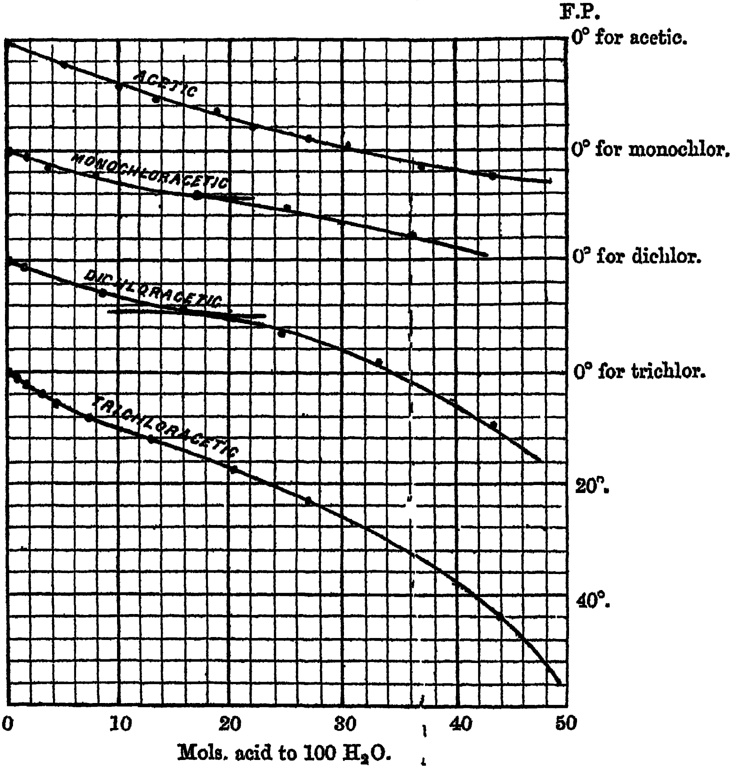
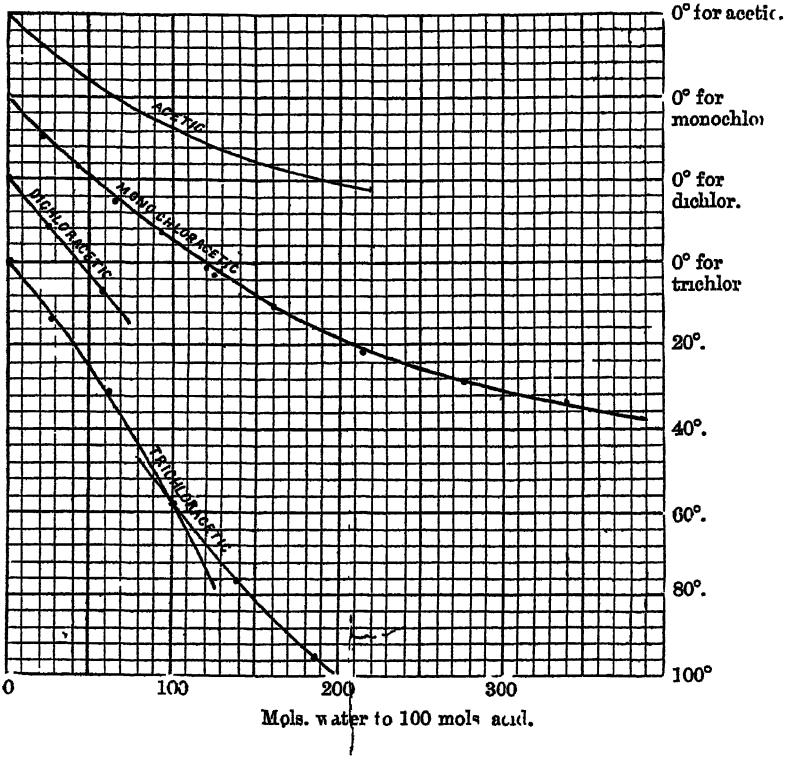


FIG. 3.—Depression of the Freezing-points of the Acids by Water.



LXXIII.—*Helium, a Constituent of certain Minerals.*

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THE gas obtained from the mineral clèveite, of which a preliminary account has been communicated to the Royal Society (Proc., May 2nd, 1895), has been the subject of our investigation since the middle of April. Although much still remains to be done, enough information has been gained to make us believe that an account of our experiments, so far as they have gone, will be received with interest.

We have attempted to ascertain, in the first place, from what minerals this gas, showing a yellow line almost, if not quite, identical in wave-length with the line D_3 of the chromospheric spectrum, and to which one of us has provisionally given the name "helium"—a name applied by Professors Lockyer and Frankland some 30 years ago to a hypothetical solar element, characterised by the yellow line D_3 of wave-length 5875·982 (Rowland). We may state at once that it is not our purpose to attempt to prove this coincidence, but willingly to leave the subject to those who are more practised in such measurements.

We propose therefore, first, to discuss the terrestrial sources of this gas; second, to describe experiments on products from several sources; and last, to propound some general views on the nature of this curious substance.

I. *The Sources of Helium.*

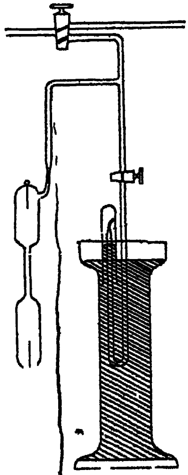
It is usual in a memoir of this kind to cite previous work on the subject. It would be foreign to our purpose to discuss observations on the solar spectrum; our memoir deals with terrestrial helium. And we have been able to find only one short note of a few lines on the subject; it is a statement by Signor Palmieri (*Rend. Acc. di Napoli*, **20**, 233), that on examining a lava-like product ejected by Vesuvius, he found a soft substance which gave a yellow spectral line of wave-length 587·5; he promised further researches, but, so far as we know, he did not fulfil his promise. He does not give any details as to how he examined the mineral.

An account has already been given in Part I of Dr. Hillebrand's investigations on the gases occluded by various uraninites which he was so unfortunate as to mistake for nitrogen. Dr. Hillebrand was so kind as to supply us with a fair quantity of the uraninite he employed; and it is satisfactory to be able to confirm his results so far; for it is beyond doubt that the gas evolved from his uraninite by heating it in a vacuum or by boiling with sulphuric acid contains about 10 per cent. of its volume of nitrogen. It is therefore not to be wondered at, that he formed the conclusion that the gas he had was nitrogen; for he obtained some evidence of the formation of nitrous fumes on passing sparks through a mixture of this gas with oxygen; he succeeded in obtaining a weighable amount of ammonium platinochloride from the product of sparking it with hydrogen in presence of hydrochloric acid; and, in addition, he observed a strong nitrogen spectrum in a sample of the gas transferred to a vacuum-tube. Had he operated with clèveite, as will be shown later, he would have in all probability discovered helium (*Bull. U.S. Geological Survey*, **78**, 43).

To extract the gas from small quantities of minerals, from 2 to 5 grams of the coarsely powdered substance was heated in a small bulb of combustion tubing, previously exhausted by a Töppler's pump. As it was found that water and carbon dioxide were often evolved, a soda-lime tube and a tube filled with phosphoric anhydride were often interposed between the bulb and the pump. After most of the gas had been evolved, the temperature was raised until the hard-glass bulb began to collapse.

Many of the minerals evolved hydrogen; hence, after the gas had entered the pump, the bulb was completely exhausted, and the gas was sparked with oxygen, no alkali being present. The oxygen was then absorbed with caustic soda and pyrogallic acid, and the gas was transferred to a vacuum-tube. As this process of transference proved very convenient, it is worth while to describe it in full.

The apparatus is shown in the annexed figure. It consists of a tube provided with a perfectly-fitting stop-cock; this tube is connected with a Töppler's pump. The vacuum-tube or tubes to be fitted are sealed to a lateral branch above the stop-cock. The lower part is bent into a sharp U, and the end drawn out to a point and sealed. The stop-cock is then turned full on, and the whole tube is completely exhausted, until the vacuum-tube shows brilliant phosphorescence, or, indeed, as often happens, ceases to conduct the discharge; the stop-cock is then closed. A mercury trough is placed below the bend of the tube, and the latter is sunk until the closed end disappears below the mercury. A small tube, which need not contain more than 1 c.c. of the gas to be introduced into the vacuum-tube, is then placed over the closed end of the bent tube, and the mercury trough is lowered. The sealed end is then broken by pressing it against the interior of the gas-tube, when gas enters up to the stop-cock. On carefully opening the stop-cock a trace of gas is passed into the vacuum-tube; this gas is then pumped out and col-



lected below the delivery tube of the Töppler's pump. One such washing with gas is usually sufficient. The stop-cock is again opened, and a sufficient amount of gas introduced into the vacuum-tube to show the spectrum. The vacuum-tube is then removed by sealing, and the gas still remaining in the bent tube may be transferred to the pump and collected. It is seen that this method permits of the filling of a vacuum-tube absolutely without loss, and it may be added with great expedition.

The results obtained with the minerals examined are given in the table on the following page.

The spectrum of helium is characterised by five very brilliant lines; these occur in the red, the yellow, the blue-green, the blue, and the violet. In every case, except with hjelmite, fergusonite, and xenotime, in which cases the lines were merely seen, all these lines were identified by simultaneous comparison in the same spectroscope with the spectrum of helium from clèveite. With the gas from samarskite and in some other cases a still more careful comparison was made, and the absolute coincidence of every visible li was ascertained. nate

From many of these minerals, a hydrocarbon was extr ium. his was manifested by the non-absorption of the gas by c nparatively h until after explosion with oxygen. It would be intes ither clèveite . tain whether the hydrocarbon is present as such in te formed during the heating, for in all cases where a gh of helium. was evolved, a large quantity of hydrogen was also obtained. taining If a vacuum-tube be charged with the crude gas, merely deprived of carbon dioxide by caustic alkali, the spectrum consists almost wholly of the fluted bands of carbon.

It is here of interest to inquire which constituent of these minerals is effective in retaining helium. For this purpose, it is necessary to know their composition; but it has not been possible to make accurate analyses of all the samples of minerals treated. Hillebrand supposed that the gas was retained by the uranium, and states that its volume varies roughly with the amount of uranium oxides present. To decide the question, it is necessary to consider the composition of these minerals in some detail.

Yttrotantalite is essentially a tantalate of yttrium and calcium, containing a little tungstic acid, and small amounts of iron and uranium. The yield of helium was here small.

Samarskite is a niobate of uranium, iron, and yttria, containing smaller amounts of tungsten, zirconium, and thorium. The amount of uranium oxide is about 11 or 12 per cent.; of thorium oxide about 6, of yttrium 13, and of cerium 3. It yields a moderate amount of helium.

Name of mineral.	Source.	Result.
Yttrotantalite......	Rachwane, Ceylon	Hydrogen and helium.
Samarskite	Unknown	A little hydrogen and nitrogen. After sparking with oxygen over caustic soda, 15 grams yielded approximately 4 c.c. of helium. At high pressure (4 mm) the unsparked gas shows fluted carbon spectrum. At low pressures this is invisible.
Hjelmite	Fahlun, Sweden	No hydrogen; trace of helium.
Fergusonite	Ytterby, Sweden	" "
Tantalite	Fahlun, Sweden	Trace of helium.
Pitchblende.......	Cornwall..............	50 grams yielded about 0·5 c.c. of helium. After fusion with hydrogen potassium sulphate, a further very small quantity was obtained.
Pitchblende	Unknown	Small quantity of helium.
Polyc e	Hitterö, Norway.........	" "
	All these minerals contain uranium.	
Mo	N. Carolina	Contains hydrogen and helium in fair quantity.
	Fahlun, Sweden	Do. do.
	Bahia......	Do. do.
	Skrotorp, near Moss, Norway	Do. do.
Aeu.	Brazil..................	Hydrogen, and, after explosion with oxygen, a trace of helium.
Orangeite	Near Arendal	Easily gave a good spectrum of pure helium.
Columbite	N. America.............	Much hydrogen; no helium.
Perofskite	Magnet Cove, Arkansas ..	Very little gas; partly hydrogen.
Wazite	Sweden	Hardly any gas; trace of hydrogen.
Thorite	Norway	Fair quantity of hydrogen.
Fluocerite	Unknown	Carbon dioxide - glass etched.
Orthite...........	Hitterö, Norwa	Carbon dioxide and small quantity of hydrogen.
Gadolinite	" "	
Euxenite..........	" "	Do. do.
Cerite	Unknown...............	90 grams gave 50 c.c. of gas, leaving 1·3 c.c. after explosion with oxygen. After sparking and absorbing oxygen, 0·1 c.c. remained. Not examined.
Blende...........	Unknown...............	No gas.
Rutile	"	"
Gummite	Flat Rock Mine, Mitchell co., N. Carolina.	No gas, except a trace of carbon dioxide.
Pyrolusite.........	Unknown	Only oxygen.
Native platinum ...	Brazil..................	Trace of oxygen.
" " ...	Siberia	Trace of oxygen in larger quantity, and trace of nitrogen.

Hjelmite closely resembles tantalite in composition, but contains stannic oxide. The yield of helium was minute.

Fergusonite is a niobate of yttrium and cerium, containing only a small amount of uranium, zirconium, tin, tungsten, &c. The yield of helium was here minute.

Tantolite consists of tantalate of iron and manganese; the helium obtained was a mere trace.

Pitchblende consists mainly of the oxide, U_3O_8. The rare metals are present in English pitchblende in very minute amount. The helium obtained was very minute in quantity, and had a large amount of the mineral not been used it would doubtless have escaped detection.

Polycrase is a niobate of uranium, containing titanium, iron, yttrium, and cerium. The amount of helium obta [illegible] from it was small.

These minerals, it will be seen, all contain [illegible] To them must be added clèveite and broggerite, from whicl [illegible] best yield was obtained.

Monazite, which gave a good yield of l [illegible] phosphate of cerium, lanthanum, and thorium, but does [illegible] r uranium. It might serve, if necessary, as a source of he [illegible] comparatively cheap; it would form a more economical [illegible] ither clèveite or bröggerite.

Xenotime is a phosphate of yttrium, anc [illegible] of helium.

Orangeite and *Thorite* are silicates of thor [illegible] taining small quantities of uranium and lead. The former of these yielded a fair amount of helium, but none could be obtained from a larger quantity of the latter.

From these details, it may be concluded that the helium is retained by minerals consisting of salts of uranium, yttrium, and thorium. Whether its presence is conditioned by the uranium, the yttrium, or the thorium, we are hardly yet in a position to decide. To judge by the Cornish ore, oxide of uranium alone is sufficient to retain it; but that its presence is not absolutely necessary is shown by its existence in monazite and xenotime. The high atomic weights of uranium and thorium, and the low atomic weight of helium suggest some connection; and yet yttrium, which possesses a medium atomic weight, sometimes appears to favour the presence of the gas; for yttrium is present in yttrotantalite, which, however, contains uranium, and in clèveite, in which uranium is present in relatively large amount.

None of the oxides of uranium, when heated in helium and allowed to cool, retains the gas; but similar experiments have not yet been made with oxides of thorium and yttrium, or with a mixture of these with uranium oxide.

II. *The Properties of Helium.*

From what has preceded, it appears that up to now only three minerals are available as sources of helium, unless, indeed, very large quantities of samarskite and yttrotantalite are worked up. These three are clèveite, the uraninite investigated by Hillebrand, and bröggerite. And here we wish to express our indebtedness to Professor Brögger for his great kindness in placing a large stock of bröggerite at our disposal. It has furnished a large quantity of the helium which we have had in our hands.

Although, so far as we were able to judge by throwing into a two-prism spectroscope of Browning's the spectra of samples of gases obtained from the minerals previously mentioned, all the specimens
of helium v identical, still a further proof was desirable. Owing
to the small of gas yielded by these minerals, amounting
in most cases c.c., it was impossible to ascertain whether
these samples e same density; but the case was different
with the gas ite and from bröggerite. In each case a
sufficient quan tained to make it possible to determine the
density with cy. It will be convenient therefore to
describe the r tracting the gas and the methods of deter-
mining its de

In the com the Royal Society it was stated that the
maximum de iginal gas from clèveite was 3·89. The
spectroscope the presence of nitrogen in this sample; the bands were very brilliant at high pressure, but on reducing the pressure the yellow line became brilliant, and the nitrogen spectrum disappeared. This always happens when the tube has platinum electrodes and a strong discharge is passed for a considerable time. An attempt was made to remove the nitrogen from this sample of gas by circulating it over red-hot magnesium; but an unfortunate accident caused the admixture of about its own volume of air, carrying with it argon, from which at present there is no known method of separating helium.

It appeared important to decide whether the gas evolved from these minerals is helium, or a compound of hydrogen and helium; for in the preliminary set of experiments the treatment was such that a hydride would have been decomposed either by sparking with oxygen or by passage over copper oxide at a red heat.

The result of experiments directed to this end is to show that no combined hydrogen is present. Gas was extracted from 19 grams of bröggerite by heating it in a combustion-tube to dull redness; the combustion-tube was connected with a Töppler's pump by means of thick-walled india-rubber tubing, wired carefully. Special experiments showed that the leakage through the india-rubber amounted between Saturday and Monday to less than one small bubble. The bröggerite yielded about 75 c.c. of gas, a large portion of which was absorbed by caustic soda, leaving about 35 c.c. A second charge of 18·3 grams gave 58·5 c.c., and a third, of 22·1 grams, gave 66·0 c.c. The amount of gas evolved depends largely on the temperature. The evolution is rapid at first, but becomes very slow after three hours, and the heating was always stopped before all the gas which might have been extracted had come off. The last portions, as will be seen later, were extracted by fusion with hydrogen potassium sulphate.

This crude product from bröggerite blackened mercury, doubtless owing to the presence of hydrogen sulphide.

The density of this sample was determined; the data are these.

Volume of bulb	3[illegible]
Temperature	[illegible]
Pressure (corr.)	[illegible]
Weight	[illegible] ram.
Density (O = 16)	[illegible]

The exceedingly small capacity of the bu [illegible] ome remark, but for no apology. The object here is, no [illegible] e the density with the utmost accuracy, but to secure [illegible] cient for our purpose, which will indicate the probable n [illegible] ht. Now the hydrogen contained in such a bulb at 0 [illegible] . weighs approximately 0·0030 gram. A sensitive balance [illegible] ing, adjusted for the special purpose, could easily be read to 0·00005 gram, without resorting to the reading of oscillations of the pointer; and this gives an accuracy of 5 parts in 300, or 1·7 per cent. Hence the density of hydrogen, thus determined, might vary between 0·983 and 1·017. It is evident that such an approximation is quite sufficient for our present purpose. The total volume of this gas was 124·5 c.c. A solution of soda was introduced by means of a pipette, and, after all absorption had ceased, the residue measured 78·0 c.c. The density was again determined.

Volume of bulb	33·023 c.c.
Temperature	21·6°.
Pressure (corr.)	765·4 mm.
Weight	0·0058 gram.
Density (O = 16)	2·105.

This gas was now left in contact with palladium sponge for a night. The sponge was made by reducing the chloride in a current of hydrogen, at a dull red heat. As it was somewhat porous, it was hammered on a steel anvil before introducing it into the gas, which, of course, was confined over mercury. The contraction amounted to about 1/30th. The density was again taken.

Volume of bulb	33·023 c.c.
Temperature	19·2°.
Pressure (corr.)	760·2 mm.
Weight	0 00630 gram.
Density (O = 16)	2·284.

This gas had undergone no treatment which was of a kind to remove combined hydrogen, unless, indeed—a very improbable assumption—it be supposed that the compound should be decomposed by contact with metallic palladium. The gas was therefore placed in contact with copper oxide, which had previously been heated to redness in a vacuum, and a tube filled with phosphoric anhydride was so interposed as to a[illegible] water produced. The gain in weight of this tube was 0·0 indicating the oxidation of about 2 c.c. of hydrogen. I bility this hydrogen had remained over after treatment wit n; for it bears no proportion to the total quantity of ga

The densit determined.

ulb	33 023 c.c.
	16·67°.
r.)	754·9 mm.
	0 00720 gram.
= 16)	2·606.

We give thus minutely all the determinations of density of such samples, because, although they refer to an imperfectly purified sample, yet they show that the density is very low, and they trace, moreover, the gradual change as one ingredient after another is removed.

The bröggerite which had been heated in a vacuum was next fused in successive portions with hydrogen potassium sulphate. A large quantity of gas was evolved, consisting of sulphur dioxide, carbon dioxide, nitrogen, and helium. The sulphur dioxide was removed with chromic mixture, and the carbon dioxide with caustic soda; the yield was 45 c.c. The density was then determined.

Volume of bulb	33 023 c.c.
Temperature	16 18°.
Pressure (corr.)	753·3 mm.
Weight	0·01035 gram.
Density (O = 16)	3·748.

No alteration in volume occurred on passing the gas for several hours over red-hot copper oxide. Hence no hydrogen was present in the free state; and if combined, passage over copper oxide does not decompose the hydride, as was seen before, when the water produced was weighed. It may be remarked that every known hydride would yield its hydrogen on such treatment.

This sample of gas was next circulated over red-hot magnesium for several hours. It is hardly necessary to state that the magnesium was first heated to redness in a vacuum so as to remove hydrogen. In case any should escape removal, however, a red-hot tube of copper oxide formed part of the circuit, as well as a tube filled with phosphoric anhydride. Some caustic soda solution was present in the reservoir above the mercury, which would have absorbed the products of combustion of any hydrocarbon present. The density of this gas was calculated from the data appended.

Volume of bulb............	33·023 c.c.
Temperature..............	14·88°.
Pressure (corr.)	756·0 mm.
Weight	0·00845 gram.
Density (O = 16)..........	3·037.

On examining the magnesium tube, after it had cooled, it was found that on moistening it ammonia was evolved. The gas was, therefore, again circulated over magnesium, at a somewhat higher temperature, so high, indeed, that the gas must have passed repeatedly through magnesium vapour. On pumping out the tubes, an accident led to the loss of a few c.c. of gas; hence the weighing bulb had to be filled at a somewhat reduced pressure. The density is given below.

Volume of bulb............	33·023 c.c.
Temperature..............	18·33°.
Pressure (corr.)............	615·8 mm.
Weight	0·0049 gram.
Density (O = 16)..........	2·187.

Again, on moistening the broken magnesium tube, ammonia was evolved; it was recognised by its odour and by its turning red litmus paper blue.

A further experiment was made with bröggerite. 30·8 grams were heated in a vacuum and the gas was collected over mercury, on to the surface of which a few c.c. of caustic soda solution were introduced. The yield of gas was 65 c.c. It was circulated over copper oxide to remove hydrogen, and its density was then determined.

Volume of bulb............	33·023 c.c.
Temperature..............	19·70°.
Pressure (corr.)............	756·7 mm.
Weight...................	0·0068 gram.
Density	2·481.

The density of this sample is almost coincident with that of a previous sample, 2·606, obtained in the same way, after it had been purified from hydrogen. This gas was next circulated over very hot magnesium, so as to remove nitrogen. Again, it is certain that for many hours the gas must have been mixed with magnesium vapour, for the magnesium had been completely volatilised out of the hot part of the combustion-tube, and had condensed at the cool end. Again, the product, when moistened, showed the reactions of ammonia, proving that nitrogen had been removed. The density of this sample was next taken.

Volume of bulb	33·023 c.c.
Temperature	19·70°.
Pressure (corr.)	756·7 mm.
Weight	0·0056 gram.
Density	2·044.

The copper oxide tube was omitted during this circulation; hence the density was low, 2·044. The spectrum of this gas showed hydrogen lines and feeble nitrogen bands. A second determination of density, in which the bulb was freshly filled, gave, at the same pressure and at a temperature differing by only 1° from the previous one, an identical weight. Further circulation for a whole day over red-hot magnesium, raised to the highest temperature which the tube could stand, gave a specimen from which hydrogen and nitrogen were absent; at least, the barest trace was visible in a vacuum-tube filled at a fairly high pressure; and care was taken to interpose a red-hot copper oxide tube, and, as usual, a tube containing phosphorus pentoxide. The effect of this circulation was to raise the density.

Volume of bulb	33·023 c.c.
Temperature	17·1°.
Pressure (corr.)	763·2 mm.
Weight	0·0060 gram.
Density (O = 16)	2·152.

It is of interest to note that this sample, procured by heating bröggerite in a vacuum, has a density practically identical with that of gas obtained by fusing bröggerite with hydrogen potassium sulphate; that sample had density 2·187.

We next proceeded to extract the gas from 6·96 grams of Swedish clèveite. When heated in a vacuum, the gas was rapidly evolved at first, more quickly than from bröggerite. About 60 c.c. were obtained, and, after treatment with soda, the residue occupied 26·3 c.c. As this was not sufficient for our purpose, and as we had already by density and spectrum proved the identity of gas evolved from bröggerite on heating, and on fusion with acid sulphate, the remaining clèveite was mixed with about five times its weight of fused and dried hydrogen potassium sulphate, placed in a tube, and heated in a vacuum. A further quantity of gas was evolved, which was at once treated with caustic soda solution. Both quantities of gas were mixed. This sample was then circulated over copper oxide for several hours, and the density was then determined with the following result.

Volume of bulb............	33·023 c.c.
Temperature..............	19·43°.
Pressure (corr.)	763·2 mm.
Weight...................	0·0061 gram.
Density	2·205.

The spectrum of this gas showed the merest trace of nitrogen, but no hydrogen. The density, it will be seen, is practically coincident with that of the gas from bröggerite. It is noteworthy that the gas from clèveite contains no nitrogen. We are absolutely certain that the presence of nitrogen in the gas from bröggerite is not to be explained by leakage of air, for the tightness of the apparatus was frequently tested during each operation.

We have therefore three determinations of density, and the mean may be taken as approximately correct to within 0·05. They are:

Gas from bröggerite by heating......	2·152
Gas from bröggerite with $HKSO_4$....	2·187
Gas from clèveite..................	2·205
Mean	2·181

All these samples of gas were now mixed and passed through the usual absorbents for nitrogen and for hydrogen, namely, magnesium, copper oxide, soda-lime, and phosphoric anhydride. The density of this sample was then determined with the larger bulb. The error due to error in weighing cannot in this case amount to more than 0·3 per cent., and is probably less. Of course, the purity of the gas would affect the result. The data are as follows.

Volume of bulb............	162·843 c.c.
Temperature............ ..	17·07°.
Pressure (corr.)	764·9 mm.
Weight	0·03057 gram.
Density (O = 16)..........	2·218.

The wave-length of sound was determined with this sample of gas in a tube 1 metre in length and 9 mm. internal diameter; the vibrating rod was 580 mm. long. We found it exceedingly difficult to procure a tube in which really good sound-waves could be shown with helium; indeed, we were on several occasions nearly despairing of gaining our object. But at last perfect waves, easily read and easily counted, were produced, and measurements were taken with the following results.

Series....	I.	II.	III.	IV.	V.	VI.	VII.
Half wave-length	98·6	98·6	97·6	98·3	100·0	98·6	97·9 mm.

Mean of all, 98·8 mm. at 18·9°.

In air, a similar series gave the numbers

Series....	I.	II.	III.	IV.	V.
Half wave-length....	36·00	36·03	36·11	35·89	36·16

Mean, 36·04 mm. at 20·1°.

The ratio of the specific heat at constant volume to that at constant pressure for air is 1·408; that for helium is—

$$\frac{(36{\cdot}04)^2\times(273+18{\cdot}9)\times 14{\cdot}479}{273+20{\cdot}1} : (98{\cdot}8)^2\times 2{\cdot}218 :: 1{\cdot}408 : \mathbf{1{\cdot}632}.$$

This sample of gas was again circulated over very hot magnesium and copper oxide for seven hours; the magnesium had no smell of ammonia when breathed on, nor did it turn red litmus paper blue until after long standing. The magnesium was mostly volatilised out of the hot part of the tube.

The *density* of this sample of gas was determined.

Volume of bulb	162·843 c.c.
Temperature..................	19·8°.
Pressure (corr.)	730·0 mm.
Weight................ .. .	0·0278 gram.
Density......................	2·133.

The wave-length of sound was re-determined in the same tube as before. The figures are

Series....	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Half wave-length	102·7	100·7	101·6	100·7	102·6	101·6	100·9	101·1 mm.

Mean of all, 101·5 mm.

The ratio of the specific heats of helium, calculated from those numbers as before, is 1·652, a sufficiently close approximation to the theoretical number 1·66. In the case of argon, the purest specimen obtained gave for the ratio 1·659; and, as remarked (in the *Philosophical Transactions*, 1895, 52), not much dependence can be placed on the accuracy of the last figure.

The result of these experiments goes to prove that the density of the gas named helium is not less than 2·13, and that it has the same claim to be considered a monatomic gas as mercury gas; or if it is a mixture, it must be a mixture of monatomic gases.

As hydrogen was often evolved along with helium from minerals, it occurred to us that if a definite ratio could be found between the helium and the hydrogen evolved by the action of acid, some idea might be gained as to the valency of helium. It would be as if, for example, hydrogen and chlorine were evolved separately from salt by sulphuric acid, instead of in combination; by measuring each, the deduction could be drawn that chlorine was univalent. Experiments made to this end showed, however, that from some minerals no hydrogen is evolved. Gas, from a sample of uraninite sent by Dr. Hillebrand, contained no trace of hydrogen. It is, of course, possible, and, indeed, not unlikely, that all hydrogen is absorbed in reducing the uranic oxide to uranous oxide. The problem then becomes a complicated one; but we hope to solve it by future experiments.

As yet but few experiments have been made with the object of inducing helium to enter into combination. Like argon, it is not attacked by oxygen in presence of caustic soda under the action of the electric discharge; indeed, this forms a good method of removing all impurities other than argon. Again, like argon, it is not affected by red hot magnesium, and it is not oxidised by copper oxide at a red heat.

As helium is evolved from clèveite and similar minerals at a red heat, an attempt was made to reabsorb it by heating the powdered mineral to redness in contact with the gas, but not to so high a temperature as that which had served to cause it to be evolved. But the attempt was fruitless; no gas was absorbed. When all the gas in the tubes had been pumped out, after they were cold, heating failed to cause the evolution of more gas.

A further experiment was made, in which metallic uranium was heated to bright redness with a blow-pipe in contact with a mixture of helium and oxygen, the latter gas being greatly in excess. But, curiously, the oxidation of the uranium was very slow, and all the helium was recovered, none having been absorbed. The conditions have yet to be discovered under which helium can be made to combine with oxides of uranium, so as to reproduce the natural product.

The Solubility of Helium.

Helium is very sparingly soluble in water. A determination made by the method previously described for argon (*Phil. Trans. A.*, 1895, 37) gave 0·0073 as its coefficient at 18·2°. The tube contained 162·3 arbitrary divisions, of which 26·0 were occupied by helium and 136·3 by water. After shaking, the volume of the helium was reduced to 25·0 divisions, and that of the water was increased to 137·3. As

137·3 absorb 1·0, 1 volume of water absorbs 0·0073 volume. The whole apparatus was jacketed with running water during this experiment.

This is the lowest solubility hitherto recorded. Generally speaking, the solubility of a gas is related to the temperature at which it condenses to a liquid, and the sparing solubility of helium points to its having a very low boiling point. Professor Olszewski has kindly undertaken to make experiments on the temperature of liquefaction of helium, and it will be interesting to find whether its boiling point does not lie below, or, at least, as low as that of hydrogen; for their molecular weights are not very different, and helium is a monatomic gas, a condition which appears to lower the boiling point.

Helium is totally insoluble in absolute alcohol and in benzene.

The Spectrum of Helium

Mr. Crookes is making an exhaustive study of the spectrum of helium, and will shortly publish an account of his work. But, as some of the deductions to be drawn later depend on the lines observed, it is necessary here to add a few words. In general terms, the spectrum has already been described. The particular point to which attention is necessary here is that at least two of the lines in the spectrum of helium, seen with a wide dispersion prism, are coincident with two of the argon lines. These occur in the red, and comprise one of each of the two pairs of characteristic argon lines. This observation has been frequently repeated, using for the purpose spectroscopes of different dispersive power, and throwing into the field both spectra at the same time, with an exceedingly narrow slit; and we may say that if not absolutely identical, the lines are so near that it is not possible with the means at our disposal to recognise any difference in position. But the relative brilliancy is by no means the same. One of the argon lines, rather faint, is coincident with the prominent red of the helium spectrum, and one of the strong red argon lines is coincident with a faint red line in the helium spectrum.

Besides these two, there is a line in the orange-red, which, though perhaps not identical, yet is very close. This line is faint in helium, but moderately strong in argon. It is much more easily visible with helium in the "negative glow" than in the capillary tube.

It may also be of interest to state that, according to Runge's observation, the brilliant yellow line of helium is undoubtedly a doublet. This was frequently observed with a grating of 14,000 lines to the inch in the spectrum of the third order. But it must also be noted that one of the lines is very faint; the other, more refrangible, is immensely brighter. The distance, judged by eye, appears to be about 1/50th part of that between the lines D_1 and D_2 of sodium. Accurate information on this last point may be looked for from Mr. Crookes, Professor Lockyer, and from many others who are interested in the probable occurrence of this element in the sun.

III. *General Conclusions.*

It cannot be doubted that a close analogy exists between argon and helium. Both resist sparking with oxygen in presence of caustic soda; both are unattacked by red hot magnesium; and, if we draw the usual inference from the ratio between their specific heats at constant volume and at constant pressure, both are monatomic gases. These properties undoubtedly place them in the same chemical class, and differentiate them from all known elements.

Although opinion is divided on the precise significance of the ratio of specific heats, 1·66, it appears to be most probable that in all cases, as in that of mercury, this ratio points to the monatomicity of the molecule. If we assume this provisionally, it follows that the atomic weight of helium is identical with its molecular weight. The molecular weight is twice the density, for the molecular weights of gases are compared with the atomic weight of hydrogen, taken as unity; hence the atomic weight of helium on this assumption is 2·13 × 2 = 4·26. But again we assume, in making this calculation, that helium is a single element, and not a mixture of elements. Before discussing this question, it appears advisable to inquire whether there is any evidence which would corroborate the deduction that it is a monatomic element. This evidence must be sought for in the properties of argon, for those of helium have not as yet been sufficiently investigated.

We know from countless examples among compounds of hydrogen and carbon that increase in molecular weight is accompanied by rise of boiling point; and it may be stated as a proved fact that a polymeride has always a higher boiling point than the simpler molecule of which the polymeride is formed. Among the substances germain to this inquiry, ozone and oxygen may be cited; the complex molecule of ozone is shown by the higher temperature at which it boils. It might be concluded with certainty, therefore, that A_2, could it exist, should have a higher boiling point than A_1.

Next, it is generally the case that the boiling point of an element, provided it has not a complex molecule like that of sulphur and phosphorus, is lower, the lower its molecular weight. There are the well-known instances of chlorine, bromine, and iodine; but if it be objected that these all belong to the same group, we may cite the cases of hydrogen, −243·5°; nitrogen, −194·4°; and oxygen, −182·7°; and we may add chlorine, −102°. If argon possessed the atomic weight 20 and the molecular weight 40, it is probable that its boiling point would lie above that of chlorine, instead of, as is actually the fact, at −187°—below that of oxygen. But, it may be objected, the boiling point is determined, not by the molecular weight, but by the density. It may be urged that the density of argon is 20, and that its molecules, like those of oxygen and nitrogen, are diatomic, in spite of the argument to the contrary from the ratio of specific heats. The answer to this objection is obvious; if this were so, its boiling point should lie above, and not below that of oxygen.

These considerations cannot, of course, be accepted as evidence, but merely as corroborative of the conclusion as regards the monatomicity of argon. If they apply to argon, they apply with equal force to helium; and if they are accepted, it follows that the atomic weight of helium is 4·26.

It is again necessary to consider the character of argon in attempting to answer the next question: Are argon and helium single elements or mixtures of elements? But before discussing it, let us consider another question: How does argon happen to occur in the air and helium only in minerals? Why is helium not present in air?

A satisfactory answer to this question is, we think, contained in a paper by Dr. Johnstone Stoney (*Chem. News*, 1895, **71**, 67). He there shows that were hydrogen to be present in air (and it might be present, in spite of the oxygen with which it could be mixed, for a small quantity would surely escape combination), it would, in virtue of the velocity of its own proper molecular motion, remove itself from our planet, and emigrate to a celestial body possessing sufficient gravitational attraction to hold it fast. Dr. Stoney suggests this explanation to account for the absence of an atmosphere and of water vapour on the moon, and for the presence of an atmosphere of hydrogen on the sun. It would also account for the absence of helium in our atmosphere, and for the presence of the chromospheric line D_3. Of course if an element can form compounds, or if it is absorbed by solids, as helium appears to be, it will, like hydrogen and helium, be found on the earth.

The inertness of these gases would favour their existence in the free state. And argon exists in the atmosphere, precisely because it forms no compounds. Similarly nitrogen is a constituent of air, because in the first place those elements with which it combines directly are comparatively rare, and also because such compounds are mostly decomposed by water; and the excess of nitrogen therefore occurs in the free state. Similarly, the occurrence of free oxygen is due to the fact that some remains over, after all or almost all the readily oxidised substances have already united with oxygen. If there exist gases similar to argon in inertness, they too may be looked for in air.

Now if argon possess the atomic weight 40, there is no place for it in the periodic table of the elements. And up to now there is no exception to this orderly arrangement, if the doubtful case of tellurium be excluded. Rayleigh and Ramsay have shown that the high density of argon can hardly be accounted for by supposing that molecules of A_2 are mixed with molecules of A_1; and excluding as untenable the supposition that argon is a compound, the only remaining suggestion is that it is a mixture. No attempts have as yet been made to test the correctness of this idea; but experiments have already been started which, it is hoped, will throw light on this question.

The density of argon is too high; to fill its place in the periodic table, between chlorine and potassium, its density should be about 19 and its atomic weight 38. We might expect the presence of another element with a density of 41 and an atomic weight of 82, to follow bromine, as argon follows chlorine; and this element would probably also be a gas, since its density would be only a little higher than that of chlorine.

But here we meet with a difficulty. There are certain lines in the spectrum of helium coincident with lines in the argon spectrum. There can be only one explanation, excluding the extremely improbable hypothesis, which is not verified in any instance, that two elements may give spectra containing identical lines. That explanation is, of course, that each contains some common ingredient. The density of helium is, however, so low, that there does not appear room for any large quantity of a heavier gas; and to fit the periodic table, the density of argon should be diminished by removal of a heavier admixture, rather than increased by removal of a lighter one.

Such are the problems which now confront us. Until more experiments have thrown further light on the subject, we regard it as labour lost to discuss the relations of these curious elements to others which find their proper place in the periodic table.

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LXXIV.—*Action of Diastase on Starch. Preliminary Notice.**

By Arthur R. Ling and Julian L. Baker.

In the year 1891, C. J. Lintner (*Zeit. ges. Brauw.*, 1891, 281) stated that on treating certain beer residues and worts with phenylhydrazine acetate, an osazone was formed which was similar in melting point and crystalline appearance to the so-called isomaltosazone which had been obtained by Emil Fischer (*Ber.*, 1890, **23**, 3687) from the product of the action of hydrochloric acid (sp. gr. 1·19) on glucose, and a little later by Scheibler and Mittelmeier (*ibid.*, 1891, **24**, 303) from the unfermentable residue of commercial glucose, named gallisin by Cobenzl and Schmitt, and also from the product of the action of dilute sulphuric acid on pure glucose. Lintner subsequently stated (*Zeit. ges. Brauw.*, 1892, 6) that he had isolated isomaltose itself, and, later, in conjunction with Düll (*Zeit. angew. Chem.*, 1892, 263), he published a detailed account of the isolation of isomaltose from the products of the action of diastase on starch. In this communication, isomaltose is described as a hygroscopic unfermentable sugar, having a very sweet taste, a specific rotatory power of $[\alpha]_D = +140$, and a cupric reducing power equal to 83 per cent. of that of maltose.

Schifferer (*Inaug. Diss. Kiel*, 1892), apparently, confirmed Lintner and Düll's observations, and, more recently, Lintner and Düll, in a paper dealing with the entire products of the action of diastase on starch (*Ber.*, 1893, **26**, 2533), have described isomaltose as a hygroscopic, intensely sweet sugar, which they have hitherto failed to obtain in a distinctly crystalline condition; it is said to ferment with yeast, but much more slowly than does maltose, to be convertible into maltose by the action of diastase, to have a specific rotatory power $[\alpha]_D = +140$, a cupric reducing power equal to 80 per cent. of that of maltose, and to form a very characteristic phenylosazone, melting at 150—153°. In a recent note (*Zeit. ges. Brauw.*, 1894, 378), Lintner states that isomaltose is not completely convertible into maltose by diastase; indeed, he now mentions that by acting on starch with oxalic acid he has obtained a modification of isomaltose (stereoisomeride), which remains unaffected when treated with diastase. Both modifications are said to yield the same osazone.

From the time when Lintner's papers, announcing the existence of an isomeride of maltose in starch transformation products, first appeared, we have made repeated efforts to isolate, either the sugar specially stated that, even under the most favourable conditions, "isomaltose" ferments much less energetically than cane-sugar, dextrose, or maltose.

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* This paper was read by Mr. A. R. Ling at the meeting of the Chemical Society on Thursday, January 17th, 1895. [Editor.]

The three succeeding papers (7), (8), and (10), appeared under the joint authorship of C. J. Lintner and G. Düll, and may for convenience be considered together, so far as their description of the preparation and properties of maltose is concerned.

We shall have occasion at a future time to consider and discuss more fully the points raised in these papers which relate to the other non-crystallisable products of starch-hydrolysis, the dextrins and maltodextrins.

It was found by the above-mentioned authors, when a conversion of starch was carried out with malt-extract or diastase in such a manner that the mixed products of hydrolysis had an opticity of about $[\alpha]_D$ 170° ($[\alpha]_j$ 189°), that, besides dextrin, scarcely anything but "isomaltose" was obtained, but it was still found convenient to employ a limited fermentation at the outset of the process of separation. In one of the papers now referred to (8), the authors attempt to show that no intermediate dextrin-like compounds exist between dextrin, having an opticity of $[\alpha]_D$ 190°, and "isomaltose" with an opticity of $[\alpha]_D$ 140°. They maintain that if these intermediate compounds exist, it ought to be possible by protracted fractionation of the mixed products of hydrolysis with alcohol, to obtain compounds of a constant rotatory power lying somewhere between $[\alpha]_D$ 140° and $[\alpha]_D$ 190°

Lintner and Dull, therefore, submitted the mixed products of a starch-conversion to a very long and tedious fractionation by dialysis and precipitation with alcohol, and found that the fractions were all ultimately referable to a rotatory power of about $[\alpha]_D$ 140° ($[\alpha]_j$ 155·1°) on the one hand, and $[\alpha]_D$ 190° ($[\alpha]_j$ 210·7°) on the other. The conclusion they draw from these experiments is that no intermediate products exist, and that the *maltodextrin*, which we described in our 1885 paper as having a rotatory power of $[\alpha]_{j3.86}$ 193·1°, has no existence as a homogeneous substance, but is a mixture of dextrin with "isomaltose." We shall on a future occasion revert to this statement of Lintner and Düll, and show why they failed to obtain our maltodextrin in this case, contenting ourselves at the present time with recording the fact that, in whatever light our maltodextrin may be regarded, it certainly cannot be a mixture of Lintner's "isomaltose" and dextrin, *as it is impossible, even under the most favourable circumstances, to prepare from it a crystalline osazone.*

The portions of the fractionated starch-products, which were obtained by Lintner and Düll with a specific rotatory power under

$[\alpha]_D$ 140°, were all united, and this crude "isomaltose" was purified by fractionation with small quantities of alcohol, and by repeated successive precipitation of the chief mass with absolute alcohol. In this manner, the acids of fermentation, ash, and other impurities were gradually removed.

In the later experiments of Lintner and Düll, the purification of the "isomaltose" was effected by dissolving the concentrated syrup in a small quantity of hot methylic alcohol, adding ethylic alcohol until a slight separation took place, and then precipitating the decanted liquid with absolute alcohol. The "isomaltose" was considered pure when the double fractional crystallisation of its osazone gave no fraction higher in melting point than 150°. The analysis of the pure "isomaltose" gave an opticity of $[\alpha]_D$ 140° ($[\alpha]_j$ 155·1°, and a reducing power equal to R 80 (κ 49·6). The molecular weight determination by Raoult's freezing method gave values lying between 340 and 363. On combustion, the "isomaltosazone" gave—

	Found.	Calculated for $C_{24}H_{32}N_4O_9$.
C	55·38	55·20 per cent.
H	6·15	6·50 ,,
N	10·95	10·77 ,,

The fact that "isomaltose" is found in starch-transformations before the appearance of maltose suggested to Lintner and Düll that dextrin, and therefore starch, is composed of "isomaltose" groups.

The existence of "isomaltose" in the products of starch hydrolysis has also been affirmed by A. Schifferer (9), and also by W. L. Hiepe (11), who confirmed Lintner's statements as to its optical and reducing properties, and the crystalline habit and melting point of its osazone.

The only additional statements of any importance in these two communications are due to Hiepe, who found that whilst "isomaltose" is completely converted into maltose on further treatment with diastase, this change takes place without any sensible increase in the specific gravity of the solution, which would not be the case if isomaltose were a maltodextrin containing 17 amylon and 3 hydrolysable amylin groups. Hiepe also found that the degree of fermentability of "isomaltose" depended largely on the variety of the yeast employed. For instance, about 60 per cent. of the "isomaltose" was fermentable with pure cultures of *Frohberg* yeast, *Saccharomyces Pastorianus I*, and *S. ellipsoideus II*, whilst *Saaz* yeast only fermented about 25 per cent., and *Saccharomyces apiculatus* had no action at all.

These experiments of Hiepe on the fermentability of the substance under discussion led to further work in this direction, and ultimately Bau (12) and A. Munsche (13) independently came to the conclusion that Lintner's "isomaltose" is a mixture of two stereoisomers, α- and β-isomaltose. The former is supposed to differ from the latter in its fermentability with yeasts of the Saaz type, whilst the β-isomeride is fermented by yeasts of the Frohberg type The two isomerides are described as yielding identical osazones, having the same melting point and the same chemical and physical properties. More recently Bau (14) has described a method for the preparation of β-isomaltose based on the above-mentioned differences of fermentability, and Lintner (15) accepts the existence of the two stereoisomerides. Prior, however (16), still regards Lintner's "isomaltose" as a homogeneous substance, and denies the existence of the two isomerides.

Early in the present year, A. R. Ling and J. L. Baker (18) made a communication to this Society, an abstract of which appeared in the Proceedings (1895, p. 3), in which it is stated that from the products of the action on starch of precipitated diastase made from a low-dried malt, they had isolated a substance having approximately the optical and reducing properties of Lintner's "isomaltose," and giving numbers agreeing with the formula $C_{12}H_{22}O_{11}$. A microscopic examination showed, however, that it contained crystals resembling those of maltose; moreover, it was found to yield octacetylmaltose on acetylation. Treatment with diastase raised the reducing power from R 81·5 to R 94·5, but the specific gravity remained unaltered during this treatment. It fermented slowly with yeast, the unfermented residue being unaltered in properties. The osazone was separable into a large fraction melting at 182—185°, resembling maltosazone in appearance, and a very small fraction melting at 145—152°. The authors suggest that the substance may possibly contain the simple dextrin, $C_{12}H_{20}O_{10} + H_2O$. When starch-paste was treated at 70° with the diastase obtained from a kiln-dried malt, and the product treated with phenylhydrazine, it gave, besides glucosazone, an osazone having the form of Lintner's isomaltosazone, and melting at 150—153°. On analysis this gave numbers corresponding to a *triosazone*. It was concluded, therefore, that a *triose*, $C_{18}H_{32}O_{16}$, is one of the products of the action of diastase on starch.

On critically examining all the published statements of Lintner and others on the occurrence of this new carbohydrate "isomaltose" amongst the products of starch-hydrolysis, it is curious to note how very little real evidence has been brought forward to prove its identity with the isomaltose of Fischer. The two substances are formed under such totally different and apparently opposed conditions (one by the continued action of strong acid on dextrose, and the other by the limited hydrolytic action of diastase on starch) that the most positive proof ought to be forthcoming before we can admit their identity. There are no indications in any of Lintner's publications that he has ever prepared, or even had in his hands, Fischer's isomaltose. He has, apparently, been content to base his proof of identity entirely on the fact that the melting point and crystalline habit of his "isomaltose" from starch-transformations correspond with the described properties of the osazone of Fischer's substance. We shall have occasion to show in the course of this paper that these very properties of the osazones are, from small disturbing causes, liable to remarkable variations, and that they certainly cannot be regarded as criteria of identity unless there is strong confirmatory evidence afforded by the examination of the original sugars in a state of purity. This confirmatory evidence, in the case of the two isomaltoses, is entirely wanting, as Fischer's isomaltose has never yet been obtained in a state of even approximate purity; and the same may be said of the apparently similar compound described by Scheibler and Mittelmeier.

We have ourselves prepared Fischer's typical isomaltosazone, and also the substance described by Scheibler and Mittelmeier, and shall have more to say about them on a future occasion. In melting point and general crystalline habit they certainly much resemble the osazone of Lintner's "isomaltose," but it is the last-mentioned substance only, and the carbohydrate giving rise to it, which we shall consider in this communication. How far the explanation which we have to give of Lintner's "isomaltose" may be found applicable to the isomaltoses of Fischer, and of Scheibler and Mittelmeier, we are not at present prepared to say.

PART II.—EXPERIMENTAL.

At the time when Lintner first commenced his series of publications on "isomaltose," we were very fully occupied with investigations of quite a different nature, and it was not until about two years ago that we were able to commence a re-examination of the whole question from Lintner's standpoint. Owing to a variety of circumstances our work had to be suspended for a time, and it was not until last autumn that an opportunity occurred of again taking up the investigation, which, from that time to the present, has been continued without any further interruption.

Our first endeavour was to prepare Lintner's "isomaltose," in such a state of purity and in such a quantity as to admit of a most searching examination of its chemical and physical properties. For this purpose a transformation of 1000 grams of well purified, air-dried potato starch was made with 60 grams of a very diastatic, air-dried malt, exactly under the conditions laid down by Lintner in his later papers, the action being stopped when iodine gave a red coloration. On analysis, the mixed products of the starch transformation were found to possess the following optical and reducing properties.

$$[\alpha]_{j3\cdot96}\ 169\cdot9\ ([\alpha]_D\ 153\cdot1).$$
$$\kappa_{3\cdot96}\ 40\cdot48$$

After evaporation, we proceeded to fractionate the products of hydrolysis, amounting to 792 grams, with alcohol in the manner described in detail later on. The sequence of these various fractionations can best be followed by reference to the accompanying table (Table I), which shows at a glance the genetic relation of the various fractionated products, and some of their leading properties, which are described more fully in the text under their respective heads.

We must at the outset allude to one very important conclusion to which all our experiments lead, as this requires to be borne constantly in mind when considering the detailed results. The entire investigation confirms in the very fullest manner the accuracy of a generalisation which we have frequently insisted on, but which has been strangely overlooked by recent workers on starch-hydrolysis. We refer to the constant relation which is always found between the specific rotatory power and specific cupric-reducing power of any portion of the fractionated products of a starch transformation.

All our previous experimental work on the fractional separation of starch-products, whether by precipitation by alcohol, by dialysis, or by fermentation, has pointed unmistakably to this mutual dependence of opticity and reducing power, a dependence which was also very clearly brought out in the earlier work of C. O'Sullivan, who was the first to demonstrate it. The nature of this relation is such that, given the specific rotatory power of any separated portions of the starch products, it is possible to calculate what its cupric reduction must be; and, conversely, when the cupric reduction is known the specific rotatory power can be predicted with equal certainty.

We have on several occasions stated the exact terms of this law, which we shall in future refer to as the "law of definite relation," but, in view of its great importance, we will once more state it.

The composition of the mixed products of a starch transformation by diastase, or of any fractionated portions of such products, can always be consistently interpreted in terms of maltose, having an opticity of $[\alpha]_{j3\cdot86}$ *150°, and a reducing power of* $\kappa_{3\cdot86}$ *61·0, and of a non-reducing dextrin having an opticity of* $[\alpha]_{j3\cdot86}$ *216°.*

This law may, for our present purpose, be regarded as a purely empirical one, and it is entirely independent of any special view which may be taken of the mode in which starch is hydrolysed, or of the nature of the intermediate products which occur between starch and maltose. All these intermediate products must, however, be subject to this law, otherwise in elaborate fractionations we should often come across fractions which do not conform to it.*

When any portion of a starch transformation is found to diverge from this "law of definite relation," it is always found on examination to be due to the disturbing presence of some other substance or substances, such as those derived from the malt extract, non-volatile products of fermentation, &c. The application of this law affords us a most valuable criterion of purity, and a check against experimental error.

One or two examples will render the foregoing statements somewhat clearer.

We will assume that a fractionated portion of the starch-products has been found to have an opticity of $[\alpha]_{j3\cdot86}$ 167·2°, and a specific reducing power of $\kappa_{3\cdot86}$ 44·4. The question arises, are those values in the definite relation demanded by the above law? As the reducing power of maltose is $\kappa_{3\cdot86}$ 61·0, the percentage of maltose apparently present, calculated from the reducing power, will be $\frac{44\cdot4 \times 100}{61} =$ 72·7. Now the specific rotatory power of a mixture consisting of 72·7 per cent. maltose of $[\alpha]_{j3\cdot86}$ 150, and of 100 − 72·7 = 27·3 per cent. dextrin with a specific rotation of $[\alpha]_{j3\cdot86}$ 216°, will be

$$\frac{72\cdot7 \times 150 + 27\cdot3 \times 216}{100} = 168\cdot0^\circ,$$

a calculated opticity but very little removed from the observed opticity of 167·2°.

On the other hand, a fractionated portion of starch-products, having a specific rotation of $[\alpha]_{j3\cdot86}$ 146·4° and a reducing power of $\kappa_{3\cdot86}$ 44·4, would be absolutely inconsistent with the "law of definite relation," as such a reducing power corresponds, as we have seen, to an opticity of $[\alpha]_{j3\cdot86}$ 167·2° instead of 146·4°.

When the properties of Lintner's "isomaltose" are submitted to the test of this law, it is found not to be in accord with it, if we take Lintner's own values for the opticity and reducing power.

Taking $[\alpha]_D$ 140° and R 80 as Lintner's values, we find that these are equivalent to $[\alpha]_j$ 156·0°, and κ 48·8. Now a reducing power of κ 48·8 requires an opticity of $[\alpha]_j = 163\cdot2^\circ$, and, on the other hand, an opticity of 156·0° requires a reducing power of 55·3, a discordance which is altogether outside the limits of error allowable. We can therefore conclude with certainty either that the "isomaltose" described by Lintner contained some impurity not due to the starch, or that the method of determining the cupric reduction is not comparable with ours. These are considerations quite outside the question of the homogeneity of "isomaltose."

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* The only limitation to this statement which we can make is in those comparatively rare cases where dextrose is formed by the long-continued action of the diastase, or where this sugar has been introduced with the malt extract employed.

Fractionation of the Products of Starch Hydrolysis.

The total amount of starch-products amounted, as we have seen, to 792 grams, having a specific rotatory power of $[\alpha]_{j3.86} = 169·9°$ and a reducing power of $\kappa_{3.86}$ 40·48.

The angle calculated from the reducing power is $[\alpha]_{j3.86} = 172·2°$, as close an agreement as can be expected when we consider that the 792 grams of starch-products contained the soluble portions of 60 grams of malt used in the transformation.

The products of hydrolysis were, in the first place, separated into two chief fractions, A 1 and A 2 (see table, Plate I), in the following manner. The syrup, containing 792 grams of A, was poured slowly, and with frequent agitation, into 11½ litres of hot alcohol of such a strength that the spirit on dilution with the syrup contained 85 per cent. of alcohol. When cold, the alcohol was poured off from the precipitate, which was then further extracted with successive portions of hot 85 per cent. alcohol in large flasks, immersed in a water bath, and furnished with upright condensing tubes.

This treatment was continued for several days, until the alcohol practically ceased to dissolve any more of the starch-products. We thus separated the original syrup A into two chief fractions, A 1, insoluble, and A 2, soluble, in 85 per cent. spirit.

Fraction A 1.—Insoluble in 85 per cent. alcohol. This fraction had a specific rotation of $[\alpha]_{j3.86}$ 202·2°, and a cupric reducing power of $\kappa_{3.86}$ 12·7. The opticity calculated from the reducing power is $[\alpha]_{j3.86}$ 202·24°, so that this fraction is strictly in accord with the "law of definite relation."

With phenylhydrazine, this insoluble portion did not give a trace of a crystallisable osazone. The weight of the fraction was 256 grams, that is, a little over 30 per cent. of the total starch-products.

As this fraction A 1 evidently did not contain any of the particular substance of which we were in search it was, for the time, put on one side.

Fraction A 2.—Soluble in 85 per cent. alcohol. This amounted to 534 grams,* and on analysis gave the following numbers:—

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* The weight of these fractions was of course slightly reduced by the loss of a small portion taken out for analysis.

$[\alpha]_{j3\cdot86}$ 156·6°. $\kappa_{3\cdot86}$ 52·99.

The specific rotation *calculated* from this κ is 159·0°.

With phenylhydrazine, this fraction gave a large yield of a crystallisable osazone, having all the appearance of "isomaltosazone."

It was now considered desirable to see how far the mean optical and reducing properties of the derivative fractions A 1 and A 2 correspond with those of the parent fraction A. This could of course be readily done as the total weight of substance in each fraction was actually known, allowance being made for the small amount of the fractions used up in the analyses.

	$[\alpha]_{j3\cdot86}$.	$K_{3\cdot86}$.
Calculated mean of fractions A 1 and A 2	171·3°	40·12
Parent fraction A	169·9	40·48

These numbers are in very close accord, and conclusively show that no decomposition or further hydrolysis of the starch-products had taken place during the long treatment with alcohol. This method of re-combination was, it will be noticed, frequently employed during the progress of this research, and afforded a valuable check on the results at certain stages.

Further treatment of Fraction A 2.—After a complete separation of the alcohol, the hot syrup, containing 534 grams of solids, was poured into 2 litres of alcohol of 95 per cent., which was maintained at the boiling point. The resulting mixture contained about 85 per cent. of alcohol, and the solution containing most of the water of the syrup, was poured off and distilled, the residue being further evaporated and then added to the main portion which was now treated with alcohol of 92·5 per cent. This treatment was effected, as usual, by digestion in the water-bath with six successive portions of 92·5 per cent. spirit, each one consisting of from 2½ to 3 litres. Each separate digestion was continued for from five to eight hours, and the total quantity of alcohol employed for the extraction of the 534 grams was 16 litres. After each treatment, the alcohol was allowed to cool before decantation and distillation.

In this manner we ultimately split up Fraction A 2 into 78 grams of B 1, insoluble in 92·5 per cent. spirit, and into 456 grams of B 2, soluble in that menstruum.

Fraction B 1.—Insoluble in 92·5 per cent. alcohol. As Lintner has stated that his "isomaltose" is much less soluble in 95 per cent. alcohol than maltose, it was expected that this residue, B 1, would contain a considerable quantity of "isomaltose." Such, however, was not the case, as it did not yield a trace of a crystallisable osazone on treatment with phenylhydrazine acetate. We contented ourselves, therefore, with an analysis of this fraction, reserving its full examination for a future time.

The opticity and reducing-power were found to be $[\alpha]_{j3\cdot86}$ 179·0, $\kappa_{3\cdot86}$ 36·1. This opticity requires an angle of 177 0°, which is sufficiently near the observed angle to bring it within the "law of definite relation."

Fraction B 2.—Soluble in 92·5 per cent. alcohol. This amounted to 456 grams having the following properties:

$[\alpha]_{j3\cdot86}$ 150·0°. $\kappa_{3\cdot86}$ 56 8.

The angle required by the above κ is 154·5°. The want of closer agreement here is due to the fact that this fraction contained about 2 per cent. of sugar directly derived from the malt used in the transformation. It will be noticed how these were ultimately separated and concentrated in subsequent fractions, C 1 and E 1 of the table.

A preparation of the osazone of fraction B 2 was made in the ordinary manner with phenylhydrazine acetate. A little glucosazone was formed, and on filtering this off and cooling the filtrate, an osazone came down in spherical aggregates of well-defined needles, which after several re-crystallisations were found to have a melting point of 149—152°.

The appearance of the osazone, as well as its melting point, corresponded to the described properties of Lintner's "isomaltosazone," with which it is no doubt identical.

Fraction B 2 appeared therefore to be "isomaltose" with a little dextrose or levulose.

At this stage, the mean properties of the derivative fractions B 1 and B 2, were again compared with the properties of the parent fraction A 2, with the following results.

	$[\alpha]_{j3\cdot86}$.	$\kappa_{3\cdot86}$.
Calculated mean of fractions B 1 and B 2.....	154·2°	53·7
Parent fraction A 2	156·6	52·99

Here again we have sufficient proof that the treatment was not modifying the properties of the substances we were dealing with, and that the separation was only due to differences of solubility in the constituents.

Having now obtained in fraction B 2 what appeared to be fairly pure "isomaltose" with a small quantity of glucose derived from the malt used in the experiment, we proceeded to submit it to further fractionation.

The solution of B 2 was evaporated down to a thick syrup, and, in order to ensure a perfectly definite strength of alcohol in the subsequent experiments, the water was determined in a weighed quantity. The whole of the syrup after being weighed was removed to a flask and treated with boiling alcohol of 98 per cent. strength, which, with the water of the syrup gave a mixture containing alcohol of 96 per cent. The amount of alcohol used in the first treatment amounted to 3·6 litres to the 456 grams of solids. After treatment for three hours in the water-bath with frequent agitation, the solution was cooled, and the supernatant liquid poured off and distilled, the residue being again treated in a similar manner with further quantities of 95—96 per cent. alcohol. In all, this treatment was repeated seven times, the original parent fraction, B 2, being thus divided into *eight* fractions of which C 1 to C 7 were successively dissolved out by 96 per cent. spirit, whilst C 8 was the residue. (See Plate I.) We give in the following table the weights of each of these eight fractions with their optical and reducing properties, and also the opticity calculated from the reducing power according to the "law of definite relation."

TABLE.—*Optical and Reducing Properties of Fractions.*

	C 1.	C 2.	C 3.	C 4.	C 5.	C 6.	C 7.	C 8.
Weight in grams..	92·2	75·07	51·25	52·44	53·53	37·22	39·32	44·41
$[\alpha]_{j3\cdot86}$	139·7°	147·1°	154·1°	153·0°	152·2°	156·2°	156·4°	162·5°
$\kappa_{3\cdot86}$	64·77	61·5	59·1	57·78	57·76	56·03	53·29	48·57
$[\alpha]_{j3\cdot86}$ calculated from κ	—	150·0°	152·4°	153·4°	153·6°	155·4°	158·3°	163·4°

Fraction C 1.—On preparing the osazone from this fraction, a very marked quantity of *glucosazone* separated while the mixture was still in the water-bath On filtering this off and allowing the filtrate to cool, it deposited an osazone in aggregates of *plates*, similar to those which are often obtained from pure maltose solutions. Re-crystallisation did not alter the form of the osazone until this had been repeated several times, when a few spherical aggregates of "isomaltosazone" could be detected. The melting point could not be raised above 184°.

Fraction C 2.—Treatment of this fraction with phenylhydrazine acetate also gave a trace of *glucosazone*, and from the cooled filtrate an osazone separated, consisting principally of *maltosazone* in aggregates of well-formed plates. Intermixed with these were a fair number of the spherical aggregates of needles corresponding to Lintner's "isomaltosazone."

On recrystallisation, however, this osazone gave an altogether unexpected result, the plate-form of maltosazone giving place to a mass of crystals in aggregates of fine needles which could not be distinguished microscopically from Lintner's "isomaltosazone." The experiment was repeated with a similar result, the maltosazone first formed showing a tendency to pass over into the "isomaltosazone" form on recrystallisation. The melting point also varied to a remarkable extent, lying between 165° and 185°, and being distinctly lowered as the osazone approached the "isomaltosazone" form.

Fraction C 3.—No glucosazone was formed on treatment with phenylhydrazine, the greater part of the osazone separating in the "isomaltosazone" form, but there were also present some aggregates of well-formed plates of maltosazone. The melting point was very constant at 165—166° during all the recrystallisations.

Fraction C 4.—The osazone of this fraction was very similar to that of C 3, but contained decidedly less of the plate aggregates. The melting point varied from 157° to 165° in the various recrystallisations.

Fraction C 5.—The osazone, several times recrystallised, showed scarcely anything but the "isomaltosazone" forms, but a very few plate aggregates were recognisable. Melting point of osazone, 158°.

Fraction C 6.—The osazone of this fraction consisted entirely of the spherical aggregates of fine needles typical of "isomaltosazone," having a constant melting point of 152—153°. Percentage of nitrogen in osazone, 10·40.

Fraction C 7.—The osazone of this fraction, like the last, was typical "isomaltosazone." The melting point was, at first, 150°, but rose to 153° after four recrystallisations.

Fraction C 8.—This was the residue left after protracted treatment with alcohol of 96 per cent. With phenylhydrazine, it yielded an osazone, separating somewhat slowly in indefinitely crystallised spherules, which, on recrystallisation, assumed the typical form of "isomaltosazone." Melting point of osazone, 150—153°.

At this stage of the fractionation, the mean angle and reducing power of all the fractions from C 1 to C 8 were determined, and the results were found to be in close accord with the opticity and reducing power of their parent fraction, B 2; thus, again, proving that no change was taking place in the starch-products by this long-continued and repeated treatment with alcohol.

In considering the nature of the osazones obtained from the fractions C 1 to C 8, it is a noteworthy fact that whereas the parent fraction, B 2, from which they were all derived, gave a perfectly typical "*isomaltosazone*" without any apparent mixture of maltosazone, yet the five derivative fractions, representing, in the aggregate, about 70 per cent, by weight, of the parent fraction, all gave indications of the plate-form of *maltosazone*. The osazones of the first two derivative fractions, C 1 and C 2, amounting to 35 per cent., by weight, of the whole, consisted, in fact, as far as microscopical appearance went, mainly of *maltosazone*.

Further consideration of Fractions C 6 *and* C 7.—As it is evident from the properties of their osazones that these two fractions must, according to Lintner's definition, be pure, or nearly pure, "isomaltose," we here, again, give their optical and reducing properties, with their equivalents in the notation adopted by Lintner.

	$[\alpha]_{j3\cdot86}$.	$\kappa_{3\cdot86}$.	$[\alpha]_D$.	R.
Fraction C 6..	156·2°	56·03	140·2°	91·8
,, C 7..	156·4	53·29	140·3	87·3

It will be observed that the specific rotatory power corresponds almost exactly with that given by Lintner for pure "isomaltose," namely, $[\alpha]_D$ 140°, but that the reducing power is decidedly higher than Lintner's number, which he has stated at various times to be R 80 or R 84. Now, as R represents the reducing power calculated as a percentage of maltose, R × 61 ÷ 100 must be the value of κ for Lintner's substance—that is, in this case, 48·8. But a starch derivative with this κ ought to have an opticity of $[\alpha]_j$ 163·2°, instead of 156·2° actually observed. In other words, the opticity and reducing power of Lintner's "isomaltose," as described by him, are not consistent with the relations that ought to exist, and which certainly do exist in any fractionated portions of starch transformation products. We believe that the difference between our numbers for the reducing power and that of Lintner is due to the method of determination of the reducing power, a point on which we shall have something to say in a future communication.

Molecular Weight of Fraction C 7.—This was determined in the usual manner by Raoult's cryoscopic method, and found to be M = 351.

Treatment of Fraction C 6 *with Diastase.*—Hiepe has stated (11) that no appreciable increase in specific gravity occurs in a solution of "isomaltose" which has been digested for a long time with diastase, although this treatment is attended by a change of "isomaltose" into maltose, as proved by the osazone test. Ling and Baker (18) also found no increase in specific gravity under the foregoing conditions. The theoretical importance of this alleged fact is very great, in view of the possible composition of "isomaltose."

If "isomaltose" really contains any dextrin or amylin group, evidence of this ought certainly to be forthcoming on treatment with diastase in a small, though sensible, rise of specific gravity. As a matter of fact, we have found, notwithstanding the above statements to the contrary, that such a rise of specific gravity does take place under these conditions, and that this increase of solids in the solution is equivalent to the amount of amylin constituent deducible from the opticity and reducing power of the "isomaltose."

We made three separate experiments with fraction C 6 to determine this point, and all of them point to an *unquestionable increase in* *solids on treatment of the "isomaltose" for 90 minutes with malt-extract at* 51—52°.

When all precautions were taken, the total increase in solids, as shown by the rise of specific gravity of a solution containing 11·886 grams of "isomaltose" per 100 c.c., amounted to 0·48 per cent. The increase actually required on the assumption that the amylin constituent of "isomaltose" has been carefully hydrolysed, is 0·451 per cent.

That the so-called "isomaltose" was completely converted into maltose by the treatment described in the last experiment is shown by the following numbers.

	$[\alpha]_{j3\cdot86}$.	$\kappa_{3\cdot86}$.
"Isomaltose" solution before digestion with diastase	156·2°	56·03
"Isomaltose" solution after digestion with diastase	150·8	60·47

Further evidence of the complete conversion was also afforded by an examination of the osazones before and after the above treatment.

Dialysis of Fraction C 6.—Before continuing the fractionation of any of the C series, it was considered desirable to ascertain if any members of this series which approached pure "isomaltose" in properties, could be differentiated by *dialysis*.

A portion of fraction C 6 was dissolved in water, and the solution made up to about 5 per cent. strength. This was placed in a dialyser, the water outside being changed at intervals of 24 hours. Each diffusate so obtained was evaporated and examined separately, the opticity, reducing power, and molecular weight being determined. The results were as follows.

	Parent fraction C 6.	1st diffusate.	2nd diffusate.	3rd diffusate.	Residue.
$[\alpha]_{j3\cdot86}$	156·2°	154·1°	155·6°	156·6	157·6°
$\kappa_{3\cdot86}$	56·03	57·6	56·6	55·7	54·4
Molecular weight (cryoscopic method)		322·0	372·0	387·0	372·0
$[\alpha]_{j3\cdot86}$ calculated from κ	155·4°	153·7°	154·8°	155·9°	157·1°

As these results showed a small amount of differentiation by dialysis, it was determined to again resort to fractionation with alcohol.

For this purpose, fractions C 6 and C 7 were united, and evaporated on the water bath. The mass so produced set quite solid on cooling, and after transference to a flask, was treated with 2 litres of boiling absolute alcohol for eight hours in the usual manner. When cold, the alcoholic solution was poured off and distilled, the residue being again treated in a similar manner with 2 litres more of absolute alcohol. This treatment was repeated three times, with the result that the united parent fractions C 6 and C 7 were further divided into four parts, F 1, F 2, F 3, and F 4, the last being the residue after successive treatment with spirit

Fraction F 1.—The 16·36 grams of this fraction had an opticity of $[\alpha]_{j3\cdot86}$ 150·7°, and a reducing power of $\kappa_{3\cdot86}$ 59·5, the opticity calculated from this reducing power being 151·6°. The osazone, in preparation, separated out in the "isomaltose" form, but the melting point was 156—157°, that is, decidedly higher than that of the parent fractions C 6 and C 7, which was 150—153°. Percentage of nitrogen in the osazone, 10·64.

Fraction F 2.—The 7·81 grams of this fraction had $[\alpha]_{j3\cdot86}$ 160·1° and $\kappa_{3\cdot86}$ 51·9. The opticity calculated from the reducing power is 159·9°. The osazone in appearance and melting point was that of typical "isomaltose."

Fraction F 3.—Weight 6·46 grams, with an opticity of $[\alpha]_{j3\cdot86}$ 158·7° and a reducing power of $\kappa_{3\cdot86}$ 52·2, the angle calculated from the reducing power according to the "law of definite relation" being 159·5°. Here, again, the osazone was that of typical "isomaltose."

Fraction F 4.—Weight 3·06 grams. Opticity $[\alpha]_{j3\cdot86}$ 159·4°. Reducing power $\kappa_{3\cdot86}$ 53·1. The angle calculated from the reducing power is 158·5°. The osazone was that of typical "isomaltose."

At this stage, the mean opticity and reducing power of fractions F 1 to F 4 were calculated, and were found to agree closely with those of the mixed parent fractions C 6 and C 7.

	$[\alpha]_{j3\cdot86}$.	$\kappa_{3\cdot86}$.
Calculated mean of fractions F 1—F 4	155·2	55·7
Parent fractions C 6 and C 7	155·9	56·0

Treatment of Fractions C 3, C 4, *and* C 5 *united.*—These three fractions, amounting together to 157 grams, had almost identical optical and reducing properties, as will be seen by referring to the table (Plate I). Their osazone had, however, a somewhat high melting point, ranging from 158° to 165°, and there was a suspicion of the presence of a trace of glucose in one of them.

After uniting these fractions, they were submitted to a very thorough differentiation with alcohol, and we regard the results obtained by the examination of their derivatives as of the highest importance in this investigation.

The united fractions were treated in the usual manner by digestion for six hours with 3 litres of boiling alcohol of 95 per cent.

strength, which differentiated them into a soluble portion E, which will be considered later on, and an insoluble portion D.

Fraction D.—This amounted to about 50 grams, and its opticity was $[\alpha]_{j3\cdot86}$ 160·5°, and its reducing power $\kappa_{3\cdot86}$ 52·2. The opticity calculated from the κ is 159·5°. The osazone crystallised in spherical aggregates of fine needles, typical of "isomaltosazone," and with a constant melting point of 153° (see Plate II, Fig. 2).

Owing to the importance which this fraction D assumed in our subsequent experiments, we prepared and studied its osazone on several different occasions, but no matter how many times it was recrystallised, the crystalline habit and melting point were unchanged, and we could never detect in it any trace of the plates and plate-aggregates characteristic of maltosazone proper. Percentage of nitrogen in osazone, 10·34.

Fraction D was now further treated with three successive quantities of hot absolute alcohol, each of 2 litres. In this way it was split up into three soluble fractions, D 1, D 2, and D 3, and a residue, D 4. These derivative fractions had the following properties.

	D 1.	D 2.	D 3.	D 4
Amount in grams	14·951	9·320	9·195	14·432
$[\alpha]_{j3\cdot86}$	153·8°	159·0	160·5°	159·7
$\kappa_{3\cdot86}$	57·6	52·7	52·2	51·0

The mean values of these fractions are $[\alpha]_{j3\cdot86}$ 157·8° and $\kappa_{3\cdot86}$ 53·7, against $[\alpha]_{j3\cdot86}$ 160·5° and $\kappa_{3\cdot86}$ 52·2 for the parent fraction D.

The yield of osazone from the parent fraction D was only 4·7 per cent. on the amount of solid taken for treatment with phenylhydrazine. The yield from fractions D 1 to D 4 was considerably more than this, but very variable in quantity, as will be seen below.

Fraction D 1.—Seven grams of this fraction gave 3·9 grams of crystallised osazone, which represents a yield of 55 per cent. Nearly the whole of the crystals separated in large, well-formed plates, in some cases singly, but for the most part arranged in aggregates around a central nucleus. It was, in fact, well-characterised *maltosazone*, with but a relatively small quantity of the spherical aggregates of fine needles which have been hitherto known as "isomaltosazone."

The melting point was low, the crude product melting at 153—155°. After one recrystallisation, this was practically unaltered, but rose to 156—158° after a fourth treatment of this kind, when it was discovered that the crystals had become changed from their original plate-form to true needle aggregates of "isomaltosazone." This curious transition of the osazone from the maltosazone to the "isomaltosazone" form led to a close examination of the conditions under which the osazone was deposited. It was found that on slowly cooling the solution of the osazone, there was evidence of the separation of a small quantity of a second substance which was apparently more soluble than the crystalline osazone, as it separated after most of this had been thrown down. The osazone was accordingly fractionated by filtering the solution whilst still warm, and further recrystallising the first portion thrown down. The crystals in this case were well-formed plate aggregates of the maltosazone type, and the melting point rose to 162—163°. When this process was repeated eight or ten times, the melting point again fell to 153—154°, although the maltosazone plate form was retained. It was evident, however, from the increased production of minute oily globules with the crystals that a decomposition of the osazone was taking place.

It was while employed on this part of our subject that the suspicion first arose that the so-called "isomaltosazone" might after all be nothing but maltosazone modified in crystalline habit and melting point by the presence of a small quantity of another substance. How fully this suspicion was confirmed will appear later on. Percentage of nitrogen in D 1 osazone, 10·68.

Fraction D 2.—Six grams of this fraction, with phenylhydrazine, yielded 2 grams of crude crystallised osazone, that is, 33 per cent. This consisted principally of needle-aggregates of "isomaltosazone," with some plate-aggregates of the maltosazone type; on the first recrystallisation, these increased in quantity, but the osazone reverted more and more to the "isomaltosazone" type on each subsequent recrystallisation. On the fourth treatment, the plate-forms entirely disappeared. The melting points were as follows.

First recrystallisation	....	145–146°
Second ,,	....	151–153°
Third ,,	....	153°
Fourth ,,	....	153°

The melting point of the plate-aggregates in this case did not differ from that of the needle-aggregates. Percentage of nitrogen in osazone, 10·10.

Fraction D 3.—The yield of osazone from this fraction was 21 per cent. The crude osazone came down in the "isomaltosazone" form with an appreciable quantity of plate-aggregates, which almost completely disappeared after several recrystallisations.

Melting point of osazone –

First recrystallisation	141—145°
Second "	144—147°
Third "	148°
Fourth "	152°
Percentage of nitrogen in osazone	10·29

Fraction D 4.—This, with phenylhydrazine acetate, yielded 25 per cent. of crude osazone, which separated in the "isomaltosazone" form, with mere traces only of the plate form.

Melting point of osazone –

First recrystallisation..........	144—146°
Second "	147—149
Third "	152—153°
Fifth "	151°
Percentage of nitrogen in osazone	10·47

A most important fact is brought out in the detailed examination of fractions D 1 to D 4. Although they are derived from a fraction D, which yielded nothing but typical "isomaltosazone," yet most of these derivative fractions give osazones which consist, wholly or in part, of groups of crystals in well-developed *plates*, which are microscopically indistinguishable from *maltosazone*. This change into the plate form is to some extent attended with a rise of melting point, but this is not invariably the case.

Notwithstanding the fact that the mean of the opticities and reducing powers of the derivative fractions D 1—D 4 was found not to differ from the same properties of the parent fraction D, yet there seemed just a possibility that this marked change in the characteristics of the osazones of the derivatives might be due to some slight chemical alteration in D, brought about by the process of fractionation.

This was put to the proof by reuniting portions of each of the Fractions D 1 to D 4 in the proportion in which they originally existed in D. When this was done, it was found that the mixture had all the original properties of D, and that the osazone was identical with that of D in every respect. *The osazones of the mixed derivative fractions had, in fact, reverted to the "isomaltosazone" form and melting point, nor was it possible by any means to make the recombined fractions yield even a trace of the plate crystals of maltosazone.* (The osazone of the recombined fractions was found to contain 10·22 per cent. nitrogen.)

Here, then was a distinct proof that a substance yielding only a typical "*isomaltosazone*" could, by suitable fractionation, be split up into a portion yielding *maltosazone*. The experiment was still more suggestive of "isomaltosazone," being nothing but maltosazone modified in its properties by the presence of another substance. It would appear also that this modifying substance, whatever it is, is somewhat less soluble in absolute alcohol than is maltose.

Before further discussing this point, we must consider the other fractionations referred to in the table (Plate I).

Fraction E.—This was the complementary portion of fraction D, soluble in 95 per cent. spirit. It amounted to 107 grams, and was further fractionated with 95 per cent. alcohol into E 1 soluble, and E 2 insoluble.

Fraction E 1.—Specific rotatory power $[\alpha]_{j3\cdot86}$ 139·7°, reducing power $\kappa_{3\cdot86}$ 63·8. These numbers point unmistakably to the presence of dextrose, which was abundantly confirmed by the osazone test. After separation of the glucosazone from the hot solution, there came down, on cooling, an osazone almost wholly consisting of plate-forms of maltosazone. This fraction was evidently a mixture of pure maltose with about 10 per cent. of dextrose. Such a mixture requires $[\alpha]_{j3\cdot86}$ 140·8 and $\kappa_{38\cdot6}$ 64·9, values in very close agreement with those actually observed.

Fraction E 2.—Opticity $[\alpha]_{j3\cdot86}$ 152·0°. Reducing power $\kappa_{3\cdot86}$ 55·7. The osazone consisted of a mixture of needle and plate-aggregates.

We have now only to consider Fraction C 8, the residue of B 2 after seven successive treatments with 95 per cent. alcohol, amounting to 40 grams. This was in the first place treated successively with two portions of hot absolute alcohol, but as the amount of substance dissolved in the second treatment was small, the strength of the alcohol was afterwards reduced to 95 per cent.

Four fractions were thus obtained, which are designated in the plate as G 1, G 2, G 3, and the residue G 4.

Fraction G 1.—Weight, 6·93 grams. $[\alpha]_{j3\cdot86}$ 156·7°. $\kappa_{3\cdot86}$ 54·5. The yield of osazone was 14 per cent., and it consisted of typical "isomaltosazone," with a constant melting point of 151°. Percentage of nitrogen in osazone, 10·12.

Fraction G 2.—Weight, 3·61 grams. $[\alpha]_{j3\cdot86}$ 161·8°. $\kappa_{3\cdot86}$ 49·8. The yield of osazone was 8·2 per cent., and it consisted of typical "isomaltosazone," melting at 153°.

Fraction G 3.—Weight, 15·76 grams. $[\alpha]_{j3\cdot86}$ 159·2°. $\kappa_{3\cdot86}$ 52·5. The yield of crude osazone was 14·5 per cent. After two recrystallisations, it came down in the form of typical "isomaltosazone," melting at 152°.

Fraction G 4.—Weight, 13·97 grams. $[\alpha]_{j3\cdot86}$ 170·6° $\kappa_{3\cdot86}$ 41·8. The yield of osazone was 15·5 per cent., and it separated in the usual spherical needle aggregates of "isomaltosazone."

The mean calculated values of the fractions G 1—G 4 gave $[\alpha]_{j3\cdot86}$

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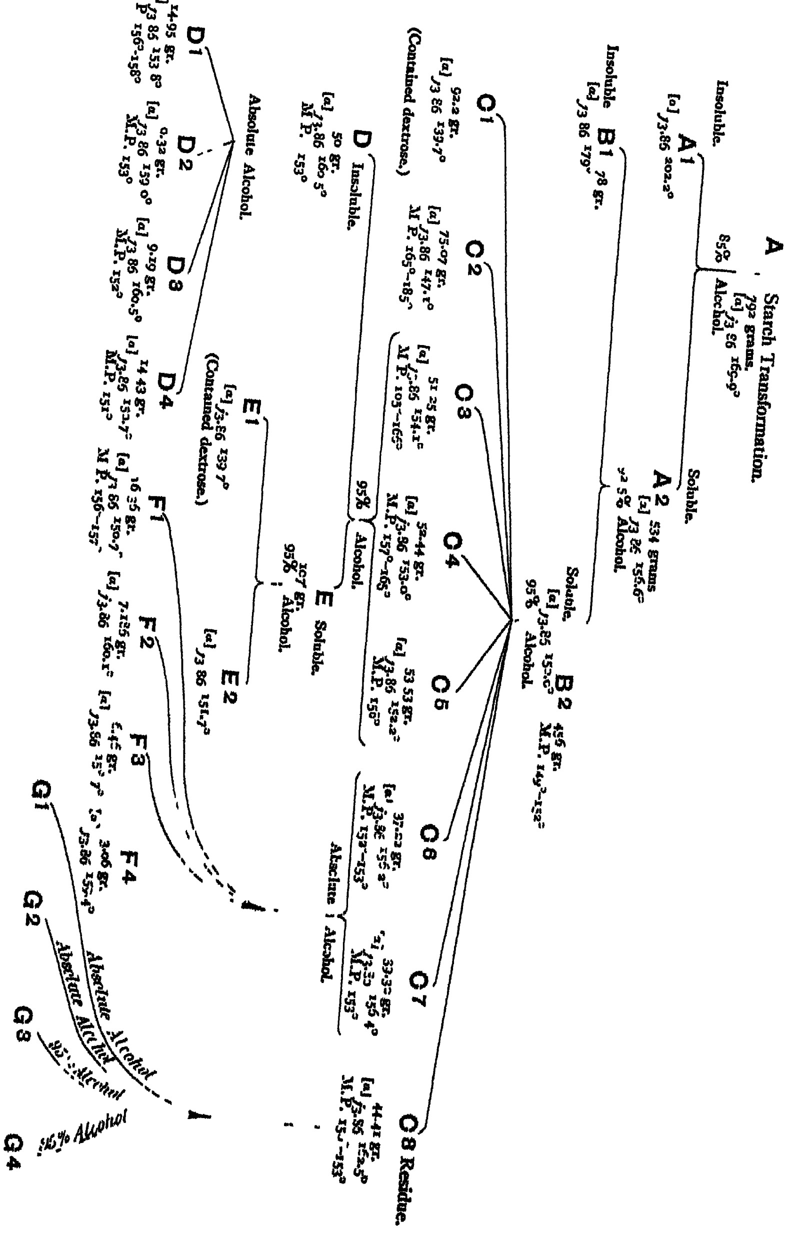
Plate I.


A Starch Transformation.
792 grams.
[α] j3.86 165.9°
85% Alcohol.
Insoluble.
A1 [α] j3.86 202.2°
Soluble.
A2 534 grams [α] j3.86 155.6°
95% Alcohol.
Insoluble
B1 78 gr. [α] j3.86 179°
Soluble.
B2 456 gr. [α] j3.85 152.0° M.P. 149°–152°
95% Alcohol.
C1 92.2 gr. [α] j3.86 139.7° (Contained dextrose.)
C2 75.07 gr. [α] j3.86 147.1° M.P. 165°–185°
C3 51.25 gr. [α] j3.85 154.1° M.P. 105°–165°
C4 32.44 gr. [α] j3.86 153.0° M.P. 157°–165°
C5 53.53 gr. [α] j3.85 152.2° M.P. 150°
C6 37.22 gr. [α] j3.86 156.2° M.P. 152°–153°
C7 33.32 gr. [α] j3.85 156.4° M.P. 153°
C8 Residue. 44.41 gr. [α] j3.86 152.5° M.P. 152°–153°
Absolute Alcohol.
95% Alcohol.
D Insoluble. 50 gr. [α] j3.86 160.5° M.P. 153°
E Soluble. 107 gr.
Alcohol.
95% Alcohol.
E1 [α] j3.86 139.7° (Contained dextrose.)
E2 [α] j3.86 151.7°
Absolute Alcohol.
D1 14.95 gr. [α] j3.86 153.8° M.P. 156°–158°
D2 0.32 gr. [α] j3.86 159.0° M.P. 153°
D3 9.19 gr. [α] j3.86 160.5° M.P. 152°
D4 14.43 gr. [α] j3.85 153.7° M.P. 151°
F1 16.55 gr. [α] j3.86 150.7° M.P. 156°–157°
F2 7.125 gr. [α] j3.86 160.1°
F3 6.45 gr. [α] j3.86 157.7°
F4 3.06 gr. [α] j3.86 157.4°
G1
G2
G3
G4
Absolute Alcohol
Absolute Alcohol
95% Alcohol
95% Alcohol

162·9°, and $K_{3\cdot86}$ 48·8, against $[\alpha]_{j3\cdot86}$ 162·5°, and $K_{3\cdot86}$ 48·5, found in the parent fraction C 8.

Fermentation of "Isomaltose."

Although much has been written during the last two or three years on the fermentability of "isomaltose," it is a very remarkable fact that no one, as far as published statements show, has taken the trouble to ascertain to what extent the unfermentable portion corresponds in optical and reducing properties with the original isomaltose taken, and with the portion fermented[*] The very fact that only 50 to 60 per cent. of a substance is fermentable by a given species of yeast under suitable conditions, ought to have suggested the probability that the substance was not homogeneous. But this is only one of several instances in the history of the later developments of the question of starch-hydrolysis, where the most obvious precautions have been neglected by those who believe that in the osazone test they have a key which will unlock all the secrets of carbohydrate transformation, with the greatest despatch, and with the least possible expenditure of trouble. Extremely useful as the osazone test undoubtedly is, as an aid to such work as we are considering, it may and does lead to great errors, if its indications are not frequently checked by a constant appeal to other older and well-tried methods.

When pure sugars, such as maltose and dextrose, are submitted to fractional fermentation, we invariably find that at any stage of the process the optical and reducing properties of the original substance, of the matter left, and of the matter fermented, agree with each other. Such, however, is certainly not the case with "isomaltose," whether this is fermented with a pure culture yeast, or the ordinary mixed yeast of our high fermentation breweries In such cases there is always a portion, sometimes amounting to as much as 50 per cent., which is quite unfermentable, and *the optical and reducing properties of this residue point to a totally different composition from that of the portion which has disappeared, or from that of the original "isomaltose."*

It is no doubt a matter of considerable difficulty to further differentiate so-called "isomaltose" with alcohol, or even by dialysis, when the rotatory power has been reduced to $[\alpha]_j$ 156 ($[\alpha]_D$ 140), but the want of homogeneity comes out at once, if we submit it to fermentation.

The following experiment, which is one of several, serves to illustrate this.

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[*] In the abstract of Ling and Baker's paper previously referred to, it is stated that the unfermentable portion of "isomaltose" has the same properties as the original substance before fermentation; up to the present time, however, we are without information as to the evidence on which this statement is based.

The fractions C 6, C 7, D 2, D 3, and D 4, consisting of so-called "isomaltose," were united. After mixing, they yielded, as before, a perfectly pure "isomaltosazone," with a melting point of 152°. The percentage of nitrogen in the osazone was 10·25.

Three hundred c.c. of a solution containing 22·64 grams of this "isomaltose" were set to ferment with about 1 gram of washed and lightly pressed yeast (the mixed yeast of a "high-fermentation" brewery). Before fermentation, the matter in solution possessed the following properties.

$$[\alpha]_{j3\cdot86}\ 159{\cdot}0^\circ. \qquad \kappa_{3\cdot86}\ 51{\cdot}7.$$

The fermentation was carried on at 28°, and was finished in three days. On driving off the alcohol from a portion taken out for analysis, it was found that 61·5 per cent. of the "isomaltose" had disappeared, and the residue now possessed the following properties.

$$[\alpha]_{j3\cdot86}\ 174{\cdot}2^\circ. \qquad \kappa_{3\cdot86}\ 38{\cdot}6.$$

By estimating the actual loss during fermentation, and the difference in opticity and reducing power before and after fermentation, it was of course easy to calculate the optical and reducing properties of the fermented substance. These were found to be

$$[\alpha]_{j3\cdot86}\ 150{\cdot}0^\circ. \qquad \kappa_{3\cdot86}\ 58{\cdot}8.$$

These last numbers, within the limits of error of this class of experiment, represent the well known properties of *maltose.*

We see, therefore, that the selective action of yeast proves beyond all doubt that so-called "isomaltose" is not the homogeneous substance it is generally supposed to be. The results are also decidedly in favour of the assumption that the readily fermentable portion of "isomaltose" is *maltose.*

Examination of the Unfermentable Portion of "Isomaltose."

In the experiment we have described above, this residue had an opticity of $[\alpha]_{j3\cdot86}$ 174·2°, and a reducing power of $\kappa_{3\cdot86}$ 38·6.

As it still gave a trace of a crystallisable osazone with phenylhydrazine, it was again submitted to fermentation for three days, with a further quantity of 0·5 gram of yeast. The residue now had an opticity of $[\alpha]_{j3\cdot86}$ 173·5°, and a cupric reduction of $\kappa_{3\cdot86}$ 38·0, *and no longer gave a trace of any insoluble osazone with phenylhydrazine.* Even with a concentrated solution, the mixture remained perfectly clear for several hours.

If the composition of this substance is expressed in terms of maltose and dextrin, we find it to be as follows.

$$\left.\begin{array}{lr}\text{Maltose........} & 63{\cdot}9\\ \text{Dextrin........} & 36{\cdot}1\\ \hline & 100{\cdot}0\end{array}\right\}\ \text{requiring}\ \begin{array}{ll}[\alpha]_{j3\cdot86} = & 173{\cdot}8^\circ\\ \kappa_{3\cdot86} & 38{\cdot}0\end{array}$$

This approaches very nearly to the composition of a maltodextrin or amyloïn, containing two *amylon* groups to one *amylin* group, but whether it is a homogeneous substance, or, as is most probably the case, a mixture of several such substances, must be left for further investigation.

The Synthetical Production of "Isomaltosazone."

It has been already noted several times during the course of this investigation, how the continued fractionation of the starch-products and the concurrent examination of their osazones, gradually led to the conclusion that *isomaltosazone* is only *maltosazone* with its crystalline habit and melting point much modified by the presence of another substance. We have repeatedly shown how a fraction yielding only pure "isomaltosazone," can be divided into separate portions, some of which yield an osazone indistinguishable from *maltosazone*, and that when such fractions are again mixed, the osazone reverts to its original "isomaltosazone" habit. Whatever the modifying influence may be, it is abundantly evident that a smaller quantity of the modifying substance is required to affect the melting point of the osazone than to influence its crystalline form, since we can have an osazone composed entirely of aggregates of well-formed plates of maltosazone with a melting point only a very little higher than that of "isomaltosazone," and at least 40° below the melting point of maltosazone, made from absolutely pure maltose.

Again, the nitrogen determinations, to which we shall presently refer more fully, point to the "isomaltosazone" preparations being sensibly poorer in nitrogen than maltosazone proper.

We are fully aware that a proof of the identity of the two osazones based on analytical methods only, however convincing it may be to those who have actually carried out the experiments, cannot carry the same conviction to others, no matter how detailed a description of the experiments may be given. Fortunately we have been able to completely demonstrate by *synthetical* methods the transformation of the osazone of pure maltose into the so-called "*isomaltosazone*."

When maltosazone, prepared from pure maltose, is allowed to separate slowly from its aqueous solution it is thrown down in the form of long yellow shining plates, having a melting point of 206° (see Plate II, Fig. 1). If the solution is cooled rapidly, the melting point of the osazone is only very slightly lowered, but the appearance of the crystals is somewhat altered. Instead of the long interlacing flat plates, the greater part separates out in fairly compact aggregates of thin plates arranged round a central nucleus.

In describing the properties of fraction D, we had occasion to note that on treatment with phenylhydrazine, after the complete separation of the crystallisable osazone, a small quantity of perfectly amorphous substance separated from the solution. It was found that the addition of a very small quantity of this amorphous substance to a hot solution containing a relatively large amount of pure maltosazone so far modified the latter that it separated on cooling in aggregates of plates, with a constant melting point as low as 165—166°, that is about 40° lower than the melting point of pure maltosazone. Both in appearance and melting point this modified maltosazone agreed with the osazone of fraction D 1 (see Plate II, fig 3).

This observation led us to a further series of experiments which enabled us to so far modify pure maltosazone that in crystalline habit, melting point, and elementary composition it is indistinguishable from Lintner's "isomaltosazone."

We have already described the properties of the residue obtained on submitting a solution of "isomaltose" to fermentation, and have stated that it amounted to 40 per cent. of the original substance, and did not yield a trace of crystallisable osazone with phenylhydrazine, even under the most favourable conditions.

To portions of this residue were added varying proportions of perfectly pure crystallised *maltose*, the solutions being afterwards treated with phenylhydrazine in the ordinary manner. Owing to the great importance we attach to these experiments we here give them in detail.

Experiment A.—1·15 gram of the unfermentable residue of "isomaltose" with an equal quantity of pure maltose. The opticity of the mixture was $[\alpha]_{j3\cdot86}$ 161·6°, that is about the same as that of the isomaltose before fermentation. This was treated with 2 grams of phenylhydrazine, and a crystallised osazone separated out on cooling in spherical aggregates of fine needles which were not altered in appearance by repeated recrystallisation. The melting point of the crude product was 145—147°, which rose to 152—153° in the second recrystallisation, remaining constant at that point. Percentage of nitrogen in the osazone, 10·22. This osazone, although it is undoubtedly derived from *maltose*, corresponds in all respects with Lintner's "*isomaltosazone*," with which is is doubtless identical (see Plate II, fig. 4).

Experiment B.—The proportion of maltose to unfermentable residue was here increased, namely, 1·15 gram of residue with 1·91 gram of maltose. The opticity of the mixture was $[\alpha]_{j3\cdot86}$ 158·6°. Treated with 3 grams of phenylhydrazine and the same amount of water as in A, it yielded an osazone in the form of sphærocrystals of typical "isomaltosazone." On recrystallisation, the melting point became constant at 168°. Percentage of nitrogen in osazone, 10·61.

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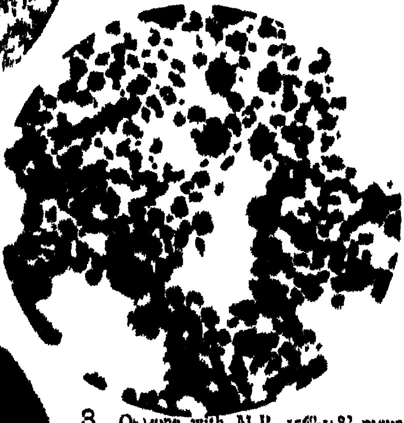
Plate II.

1

1 Maltosazone from pure maltose. M.P. 206°

2 "Isomaltosazone" of Fraction D. M.P. 153°

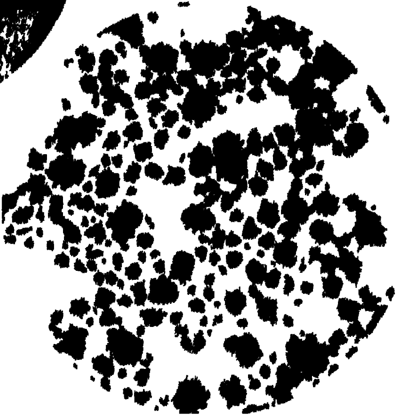


2

3

3 Osazone with M.P. 166°–168° prepared from Fraction D 1, which is a derivative of Fraction D. These plate aggregates have the crystalline habit of maltosazone, but their low melting point shows them to be still slightly impure. The Fraction D 1 yielding this osazone was a derivative of Fraction D, which was itself a typical "isomaltose."

4 Artificial "isomaltosazone" M.P. 152–153° This was prepared from a pure maltosazone similar to that of 1, by recrystallizing it from the liquid obtained by treating the non-fermentable portion of "isomaltose" with phenylhydrazin acetate. This liquid, before the addition of the maltosazone, did not yield a trace of crystallizable osazone. This osazone is indistinguishable in appearance and melting point from Lintner's "isomaltosazone."



4

Experiment C.—1·15 gram of unfermentable residue with 2·68 grams of maltose. Opticity of mixture, $[\alpha]_{j3\cdot86}$ 156·9°. On treatment with 3 grams of phenylhydrazine, the greater part of the osazone separated in typical needle aggregates of "isomaltosazone," but on the second recrystallisation there were distinct signs of plate aggregates. Melting point, 169°. Percentage of nitrogen in osazone, 10·81.

Experiment D.—1·15 gram of unfermentable residue with 3·45 grams of maltose. Opticity of mixture, $[\alpha]_{j3\cdot86}$ 156°. Treated with ·45 grams of phenylhydrazine, the crystallised osazone separated as a mixture of perfectly typical "isomaltosazone" with plate aggregates of maltosazone. Melting point, 174—177°, which was further raised by repeated recrystallisation to 185—190°. Percentage of nitrogen in osazone, 10·82.

By gradually increasing the proportion of maltose to the unfermentable residue of "isomaltose" we have, in these experiments, obtained a series of osazones exactly comparable with those obtained during the fractionation of so-called "isomaltose," and with properties varying from those of "isomaltosazone" to mixtures of this with maltosazone.

This synthetical production of "isomaltosazone" is in complete agreement with all our other observations made during fractionation of the products of starch-transformation, and confirms in every way the opinion which we had formed from the analytical processes that the constituent of "isomaltose," which yields a crystallisable osazone, is nothing more than *maltose*, and that "isomaltosazone" is merely maltosazone modified in crystalline habit and melting point by the presence of another substance derived from the action of phenylhydrazine on the maltodextrin or amyloïn constituent of "isomaltose."

In order to bring about this change of maltosazone into the "isomaltosazone" form, it is by no means necessary to treat the mixture of the modifying substance and maltose simultaneously with phenylhydrazine. The same result can be attained by merely recrystallising pure maltosazone in the clear liquid obtained by previously heating the unfermentable residue with phenylhydrazine and acetic acid. The maltosazone then comes down in the needle aggregates of "isomaltosazone," and with the melting point of 151—152°, provided the maltosazone has not been added in too great an excess. If the quantity of maltosazone bears too great a proportion to the modifying substance, the recrystallised osazone has its melting point somewhat above 152°, and may also show indications of plate forms along with the aggregates of needles.

The substance so modifying maltosazone is not the unaltered maltodextrin itself, but the product of the action of phenylhydrazine on this. This is proved by the fact that maltosazone can be crystallised out of a solution of the dextrinous unfermentable residue entirely unchanged. It is almost certain, therefore, that the modifying substance is a soluble osazone of these maltodextrin or amyloïn substances, and it is quite possible that there may even be some molecular combination of these osazones in "isomaltosazone." This is, however, quite hypothetical and scarcely seems probable looking at all the results of these experiments. If this is the fact, it is quite a different matter from the assumption that "isomaltose" is itself a chemical entity. Its behaviour on fermentation, apart from all other considerations, clearly shows that this is not the case.

Modification of Maltosazone by the Osazone Derivatives of Maltodextrin.

Pending a more complete examination of the true nature of the unfermentable portion of "isomaltose" fractions, which is almost certainly that of a maltodextrin, it seemed desirable to ascertain how far maltosazone could be modified by the osazone of the typical maltodextrin which we described in 1885 (Trans., 1885, **47**, p. 562) in our paper on the non-crystallisable products of starch-hydrolysis. It will be remembered that this substance was shown to have a composition indicating one amylon or maltose group in combination with two amylin or dextrin groups, its specific rotatory power being $[\alpha]_{j3\cdot86}$ 193·1°, and its reducing power, $\kappa_{3\cdot86}$ 21·1. C. J. Lintner and Schifferer failed to find it amongst the products of starch-hydrolysis for reasons which we shall give in a future communication, and they have assumed, without a shadow of proof, that our maltodextrin must be a mixture of dextrin with their "isomaltose." It will suffice to say at the present time that this view, even from their standpoint, is an erroneous one, *since carefully prepared maltodextrin does not yield a trace of a crystallisable osazone with phenylhydrazine.*

If any definite osazone is formed from maltodextrin under these circumstances it is non-crystalline and very soluble in water. The products of the reaction with phenylhydrazine, whatever they may be, have however the same curious property of modifying maltosazone to "isomaltosazone" as is possessed by the unfermentable residue of "isomaltose" itself.

In other words, if a mixture of typical maltodextrin and pure maltose is submitted to the osazone test the resulting maltosazone separates out with the low melting point, and spherical needle aggregates of so-called "isomaltosazone."

Three experiments were made on this point, using mixtures of maltodextrin and maltose containing 58, 70, and 77 per cent. of maltodextrin respectively. In all these cases, the osazone was typical "isomaltosazone," with a constant melting point of 156°.

Consideration of the Constitution of the so-called "Isomaltosazones" from the Percentage of Nitrogen which they contain.

In the following table we have brought together all the cases in which we determined (by Dumas' method) the nitrogen in the osazones, and have also indicated for purposes of comparison the appearance and melting point of the respective osazones.

Nitrogen in Osazones.

	Melting point.	Percentage of nitrogen.
Pure maltosazone, found	206°	10·70
" calculated for $C_{24}H_{32}N_4O_9$	—	10·77

	Microscopical appearance of osazone.	Melting point.	Percentage of nitrogen.
Fraction D.	Typical "isomaltosazone"	153°	10·34
" D 1.	Well-formed plate aggregates of maltosazone	156—158	10·68
" D 2.	Needle aggregates of "isomaltosazone" with a mixture of plate aggregates of maltosazone. Reverted to "isomaltosazone" form on several recrystallisations	153	10·10
" D 3.	Osazone of the same character as that of D 2.	152	10·29
" D 4.	"Isomaltosazone" form with some traces of plate aggregates	151	10·47
Fractions D 1, D 2, D 3, & D 4 mixed.	Typical "isomaltosazone"	151	10·22
Fraction C 6.	" "	152 153	10·40
" F 1.	" " (? some plate aggregates.	156 157	10·64
" G 1.	" "	151	10·12
" G 2.	" "	152	10·60
" G 3.	" "	152	10·75
Residue G 4.	" "	153	9·79

Artificial "Isomaltosazones" made from mixtures of the unfermentable residue *of "Isomaltose" with varying proportions of Pure Maltose.*

	Melting point.	Percentage of nitrogen
	°	
A (50 per cent. unfermentable residue, 50 per cent. pure maltose)— Typical "isomaltosazone"	152—153	10·22
B (37 per cent. unfermentable residue, 63 per cent. maltose)— Crystalline form of "isomaltosazone"	168	10·61
C (30 per cent. unfermentable residue, 70 per cent. maltose)— Typical "isomaltosazone" with mixture of plate aggregates of maltosazone....................	169	10·81
D (25 per cent. unfermentable residue, 75 per cent. maltose)— Mixture of "isomaltosazone" and maltosazone forms	174—177	10·82
Mixed fractions C 6, C 7, D 2, D 3, D 4 before fermentation— Typical "isomaltosazone"	152	10·25
"Isomaltosazone" prepared direct from a starch-transformation— Typical "isomaltosazone"	152	9·52

It is clear from the above results that typical "isomaltosazone," so-called, contains a sensibly smaller percentage of nitrogen than pure maltosazone. This is shown by the analysis of the osazones of fractions D, D 2, D 3, C 6, G 1, and also by the "artificial isomaltosazone" of Experiment A. The average percentage of nitrogen in these cases is 10·24, as compared with 10·77 for pure maltosazone.

As the substance modifying the maltosazone is more and more eliminated by careful fractionation of the original "isomaltose," and the crystalline habit of the resulting "isomaltosazone" approaches more nearly that of pure maltosazone, the nitrogen percentage rises *pari passu*, even when the melting point has not been sensibly raised.* This is shown in the above table in the case of the osazones of Fractions D 1, D 4, and F 1; also in the "artificial isomaltosazones" B, C, and D, where the added maltose exceeds 60 per cent. of the mixture from which the osazones were prepared.

Where the processes employed have still left a considerable amount of the substance which modifies the maltosazone, the nitrogen of the osazone may be lower even than 10 per cent. This is well shown in the osazone of fraction G 4 in the above table. This fraction, which was a residual one, had an opticity of $[\alpha]_{j3\cdot86}$ 170·6°, and therefore contained a considerable amount of the dextrinous bodies. The osazone, after repeated crystallisations, had all the usual properties of isomaltosazone, and contained only 9·79 per cent. of nitrogen.

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* We have already called attention to the fact that the melting point of maltosazone is more readily influenced by the presence of a small quantity of this foreign substance than is the crystalline habit.

In another case where the osazone (typical "isomaltosazone") had been prepared directly from a starch-transformation without previous fractionation, and, therefore, in the presence of a considerable excess of the modifying substances, it contained only 9·52 per cent. of nitrogen.

In conclusion, we must express our best thanks to Mr. J. H. Millar for the careful and able manner in which he has worked out, under our guidance, the details of this investigation.

Our thanks are also due to Dr. W. J. Russell and Dr. Chattaway, who kindly gave us facilities for performing the combustions of the osazones in their laboratory.

General Conclusions.

1. When the products of a starch-transformation by diastase are submitted to any known process of fractionation, the properties of each and every fraction strictly conform to the "law of definite relation" of opticity and reducing power.

2. Lintner's "isomaltose" is not a chemical entity, but can be further split up by careful fractionation with alcohol, and by fermentation, in such a manner as to indicate that it is a mixture of *maltose* and dextrinous compounds of the maltodextrin or amyloïn class. We must, therefore, from now cease to use the term "isomaltose" as applied to any of the products of the diastatic conversion of starch.

3. The crystallisable osazone which Lintner has described as "isomaltosazone," and upon which he has mainly founded his belief in the existence of "isomaltose," is nothing but *maltosazone* modified in its crystalline habit and melting point by the presence of small but varying quantities of another substance.

4. The substance or substances which are capable of thus modifying maltosazone are the products of the reaction of phenylhydrazine on the dextrinous compounds mentioned in 2.

5. This can be shown: (1) *analytically* by careful fractionation of the starch-products with alcohol, and also by fermentation; and (2) *synthetically* by the recrystallisation of pure maltosazone in the

presence of the non-crystallisable products of the action of phenylhydrazine on the maltodextrin.

6. The only substance amongst the products of starch-transformation by diastase, which is capable of yielding a crystallisable osazone, is *maltose*.

7. The results of this investigation bring out very clearly the danger of attempting to identify carbohydrates in mixtures of these substances solely by the properties of their osazones, as these properties are liable to considerable modification by the presence of other compounds of the same class, which may not in themselves be crystallisable or readily separable from aqueous solutions.

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* This paper was read January 17, 1895, and appears in the Transactions, 1895, pp. 702—708.—[EDITOR.]

LXXVI.—*Action of Diastase on Starch. Second Notice.**

By Arthur R. Ling and Julian L. Baker.

In an article published in the *Zeitschrift fur das gesammte Brauwesen*, (1895, 18, 70), C. J. Lintner refers to a report of our work which appeared in the *Chemiker Zeitung*. It is needless to enter into all the various points touched on by Lintner in this criticism, as he himself admits that it is impossible to judge how far so brief an abstract as that published in the *Chemiker Zeitung* represents our results. Suffice it to say, therefore, that Lintner regards our results as confirming rather than refuting the existence of isomaltose. Although we fail to see how he could arrive at such a conclusion from the data to hand, we believe that if the whole of our experimental evidence is taken into account (see preliminary notice, p. 702), the fact is placed beyond doubt that the substance having the properties ascribed to it by Lintner, and regarded by him as isomaltose is not a homogeneous compound. At the same time we feel that it is only fair to admit that Lintner was to some extent justified in his conclusions; thus the supposed isomaltose, when submitted to the cryoscopic method, gives indications showing that it has the same molecular weight as maltose. When prepared, however, by the agency of the diastase of low dried malt it does not, as we have shown, yield the osazone (m. p. 150—153°) which, according to Lintner, is isomaltosazone, but the product obtained from it is merely maltosazone (see also later on in this paper). Had Lintner worked with diastase prepared from low-dried malt he would not have obtained an osazone of definite melting point from the supposed isomaltose.

As regards our suggestion that isomaltose contains the simple dextrin, $C_{12}H_{20}O_{10} + H_2O$, we may say that all the experiments which we have made up to the present time and which are described in this paper, certainly furnish strong support in favour of such a view. The formula, $C_{12}H_{20}O_{10} + H_2O$, was suggested for the dextrin constituent of isomaltose, because it was in harmony with the analyses and cryoscopic determinations made with the mixture—"isomaltose." But assuming that the supposed dextrin does contain 1 mol. of water, we cannot at present say how this is combined. It seems not unlikely that what has been called by us the simple dextrin, $C_{12}H_{20}O_{10} + H_2O$, is an intermediate compound in the hydrolysis of the dextrins into maltose, and that it is formed by the addition of a molecule of water to a single dextrin group. Such a view obtains support from the fact that by the further action of diastase "isomaltose" is converted into maltose.

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* An account of the work published in our preliminary paper was read at a meeting of the Chemical Society held on January 17th, 1895, and a short abstract of it was published in the Proceedings (No. 146, 3); the paper in full is given on p. 702 of this vol.

Before describing our experiments, we wish to give the following description of our *modus operandi*:—The optical rotatory powers recorded in this paper and in our previous communication were determined with the aid of the so-called half shadow quartz-compensating polarimeter having a Ventzke scale and employing ordinary white light. The advantages of this instrument, where comparative results only are needed, over those employing monochromatic light are that it permits of easy and rapid manipulation, and that dark and opalescent solutions occasionally met with may be read with ease. The factor used for the conversion of degrees Ventzke into angular degrees (sodium light) was 0·344. (Compare Rimbach, *Ber.*, 1895, **27**, 2282.)

The cupric reducing powers were conducted according to Wein's instructions,* and the results calculated as per centage of maltose by the tables constructed by the same author, the symbol R being used to express the reducing powers in these terms.

In the preparation of the osazones, the phenylhydrazine acetate (phenylhydrazine base freshly mixed with 50 per cent. acetic acid) was heated with the sugar solution for at least two hours.

Preparation of Diastase.—The method adopted for the preparation of the diastase used in our experiments is very similar to that described by Lintner (*J. pr. Chem.*, 1886, [2], **34**, 378). Ground malt (200 grams) is digested with 20 per cent. alcohol (3 parts) for 24 hours. To the clear, brownish filtrate about 1·5 litres of 93 per cent. (by volume) alcohol is added, stirring meanwhile. After some time the alcohol is syphoned from the precipitate, which is collected on a filter, washed with alcohol of gradually increasing strengths, and finally with anhydrous ether, after which it is kept in a vacuum over concentrated sulphuric acid, and subsequently pulverised. Diastase so prepared varies in appearance from a white to a slightly brownish powder. When triturated with water, the greater portion passes into solution. Samples vary greatly in regard to their hydrolytic capacity. The weight of diastase, or rather of diastatic substance, obtained from malt by the above method, ranges from 1—2 per cent. of the malt employed, but occasionally larger yields have been obtained.

In our preliminary paper we stated that the osazone from the "isomaltose," prepared by the action of diastase from low-dried malt on starch melted between 160° and 170°, but that when it was fractionally recrystallised from hot water the main portion melted at 182—185°, and resembled maltosazone in appearance. We may now quote an experiment carried out on a larger scale with the same osazone. Some grams of the osazone were dissolved in boiling water, and the solution allowed to cool to 35°, at which temperature it was kept for some time; subsequently the substance which had crystallised out was collected and examined. The filtrate was allowed to cool to the temperature of the room, and the second crop of crystals also collected and examined. The portion which separated at 35° was then recrystallised in the same manner, and the operation repeated; the results are given below.

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* E. Wein, "Quantitative Bestimmung der Zuckerarten." Stuttgart, 1888.

Original Osazone. M. p. 160—170°.

		From filtrate cooled to temperature of room. M. p
Recrystallised at 35°, m. p...	167—170°	(Insufficient for the determination).
" " " ..	167—171	145—148°
" " " ..	178—180	150—152°
" 45 " ..	183—185°	160—162
" " " ..	184—185°	163—165°
" " " ..	182—183°	170—173°

The osazone, melting at 182—183°, was subsequently twice recrystallised, but the melting point remained unaltered; it had the appearance of maltosazone (see later). The osazones melting at 145—152° were too small in amount for any other determination than that of the melting point. A fraction was obtained, however, from another experiment, which crystallised in aggregates of needles and melted at 160°. This was analysed with the following result.

0·1063 gave 0·3725 CO_2 and 0·1812 H_2O. C = 55·15; H = 6·11.

$C_{12}H_{20}O_9(N_2HC_6H_5)_2$ requires C = 55·38; H = 6·15 per cent.

We merely quote this analysis as indicating that the osazone obtained from the "isomaltose" prepared with the diastase from low-dried malt has the composition of a hexabiosazone, and we regard the fractions melting at a temperature of 150—160° as impure maltosazone, such as is obtained when a mixture of maltose and a dextrin is heated with phenylhydrazine. Such an impure osazone may readily be purified by recrystallisation from hot water in the manner above indicated. The osazone obtained from the "isomaltose," prepared by the action of the diastase from low-dried malt on starch, consists entirely of maltosazone, but the osazone of melting point 150—153°, which Lintner believed to be isomaltosazone, has the composition of a triosazone and, as stated in our preliminary paper, is never obtained from the product of the action of low-dried malt on starch.

Experiments with Maltosazone.—Maltosazone was first described by E. Fischer (*Ber.*, 1884, **17**, 583) as crystallising from water in delicate yellow needles, and melting at 190—191°. Later, the same chemist redescribed the osazone as crystallising in yellow needles which are not combined in aggregates, and melting at 206° with decomposition. In our own experience, when maltosazone is prepared from what is now regarded as pure maltose, it usually melts at 185—190°; if this product is redissolved in a small quantity of boiling water, and the latter cooled to about 70°, crystals of melting point above 190° are, as a rule, obtained, whilst from the filtrate, cooled to the temperature of the room, crystals melting at about 180° are deposited. The crystals consist, in all cases, of comparatively large, flat needles, and stellate groups of needles. The two are doubtless identical, for we have never succeeded in effecting their separation, although we have made repeated efforts, and even the highest melting products examined have the same appearance. On one or two occasions we have obtained maltosazone melting above 200°.

Maltosazone was prepared in presence of an excess of acid (twice the quantity of 50 per cent. acetic acid usually employed). The recrystallised product had the usual appearance, and melted at 190—194°. No glucosazone was obtained in this experiment.

A portion of maltosazone melting above 190° was dissolved in about 80 parts of boiling water, and the solution kept boiling for 10 hours using a reflux condenser. The somewhat dark liquid was allowed to cool, and the osazone, which separated and had decreased in amount, was recrystallised, when it melted at 165°, the mother liquor being gelatinous. On being again recrystallised, the osazone melted at 185°. This experiment has been repeated and confirmed.

Preparation of Maltosazone in Presence of a Dextrin.—The following experiments were carried out by us in the latter part of the year 1893; the dextrins used gave no crystalline osazones but only jellies when treated *per se* with phenylhydrazine acetate.

1. A mixture of maltose (1 gram) and dextrin (0·25 gram) was heated with phenylhydrazine acetate as usual. An osazone was obtained, which, when recrystallised, formed clusters of needles, and melted at 185—188°.

2. A mixture of maltose (1 gram) and dextrin (0·5 gram) gave an osazone, crystallising in spherical clusters of needles, and melting at 180°.

3. A mixture of maltose and dextrin (equal parts) gave an osazone, crystallising in spherical aggregates of needles, and melting at 170—178°.

4. A mixture of maltose (1 gram) and dextrin (2 grams) gave an osazone, crystallising in spherical aggregates of needles, and melting at 165—168°.

5. A mixture of maltose (0·5 gram) and dextrin (1·3 grams) gave an osazone, crystallising in spherical aggregates of needles, and melting at 170°.

The experiments just described are copied from an old note-book just as they were entered. The osazones were all recrystallised once, but no further purification was attempted. We know, however, by our more recent experiments, that when such osazones as these are submitted to the process of fractional crystallisation already described, they yield maltosazone of the ordinary form and melting point.

When a mixture of maltose and glucose is treated with phenylhydrazine acetate, the osazones of both these sugars may be separated in a state of purity.

Experiments with the Diastase from Kiln-dried Malt.—One of the first facts noticed by us, in the course of the experiments on the action of the diastase prepared from kiln-dried malt, was the production of a small amount of glucose; we were therefore led to try the action of this diastase on maltose.

1. Maltose (1·5 grams), which had been several times recrystallised from 85 per cent. alcohol, and had a reducing power of $R_{3\cdot86} = 97\cdot5$, was dissolved in water (20 c.c.) together with 0·1 gram of the diastase. The solution was kept at 65—70° for two hours. The reducing power was then found to have increased to $R_{3\cdot86} = 105\cdot3$, indicating therefore the presence of 11·66 per cent. of glucose in the dissolved matter assumed to consist of maltose and glucose. The production of glucose was demonstrated by the formation of glucosazone.

2. Maltose (2·5 grams) and diastase (0·2 gram) were dissolved in water, the solution made up to 50 c.c., and heated at 70° for two hours, after which it was allowed to remain for 12 hours at the ordinary temperature. The solution was again made up to the containing mark at the normal temperature, and the reducing power determined. It gave R = 113·8, indicating the presence of 22·5 per cent. of glucose in the dissolved matter, the production of glucose was also established by the formation of glucosazone.

3. Maltose (2·5 grams) was dissolved in water and 5 c.c. of the filtered extract from 50 grams of kiln-dried malt and 125 c.c. of water added. The solution was made up to 50 c.c., and kept at 70° for one hour; after this, it was allowed to remain for some hours at the temperature of the room, when its reducing power, corrected for the malt extract, some of which was also submitted to the same treat-

ment as the maltose solution, was R = 103·6, indicating the production of 5·88 per cent. of glucose.

These experiments prove therefore beyond doubt that glucose is produced by the action on maltose of diastase from kiln-dried malt. We may add that we have never observed the production of glucose or any other action to occur when maltose is treated with the diastase from low-dried malt.

Action of Diastase from Kiln-dried Malt on Starch.—We have shown in our previous paper that when starch is hydrolysed under certain conditions by means of the diastase from kiln-dried malt, and the portion of the product soluble in 90 per cent. alcohol is treated with phenylhydrazine acetate, it yields a certain amount of glucosazone. A specimen of glucosazone, obtained in this way, was repeatedly recrystallised from alcohol, when it melted at 206°; it was then submitted to analysis with the following result.

0·1378 gave 0·3034 CO_2 and 0·0820 H_2O. C = 60·04; H = 6·61 per cent.

The formula $C_6H_{10}O_4(N_2HC_6H_5)_2$ requires C = 60·33; H = 6·14 per cent.

The main portion of the osazone formed under the circumstances above mentioned was soluble in hot water, and when a large quantity of it was recrystallised, the pure product was found to melt at 151°, and to have the appearance which, according to Lintner, is characteristic of "isomaltosazone." It gave, however, on analysis, values agreeing with those demanded by theory for a hexatriosazone. Inasmuch as apparently no maltosazone was obtained from the product of these conversions, we were at first inclined to think that no maltose was present. Subsequently, however, we have demonstrated the presence of maltose in a similar product. Maltosazone was therefore undoubtedly present in the crude soluble osazone, but the large mass of this osazone which we dealt with enabled us to get rid of the maltosazone by recrystallisation.

Having succeeded in obtaining a hexatriosazone from these products, we were naturally led to infer that a hexatriose is one of the products of the action of the diastase of kiln-dried malt on starch. A diligent search was therefore made for the new sugar, but although we have carefully fractionated and examined numerous similar starch conversions, we have not succeeded in isolating from them any crystalline sugar other than maltose. That glucose, which was invariably present, was not isolated, is explained by the relatively small amount in which it occurred. To give a detailed account of all these experiments is unnecessary, suffice it to say that we have examined the products obtained from several conversions in which quantities of starch amounting to 2000 grams were used, and have obtained abundant evidence of the presence of a substance having optical and reducing powers similar to those ascribed by Lintner to his so-called isomaltose. This substance invariably gave a soluble osazone melting at a temperature more nearly approaching that observed by Lintner for the supposed isomaltosazone, and, on analysing several of these, which were only prepared in small amounts, and could not therefore be purified by recrystallisation, values were generally obtained intermediate between those required for a hexatriosazone and a hexabiosazone. It is very difficult to get rid of the glucose from this particular fraction—at least by Lintner's method of fractionation, and its presence, as we shall now show, doubtless accounts for the lower melting point of the soluble osazone obtained from it, as compared with that obtained from the similar fraction (free from glucose) prepared by the agency of diastase from low-dried malt.

Taking into consideration the fact that evidence of the production of a hexatriosazone was obtained only in those cases in which glucose was present, together with our suggestion that so-called isomaltose contains the simple dextrin $C_{12}H_{20}O_{10} + H_2O$, it occurred to us that the hexatriosazone might be produced by the condensation of the dextrin and glucose in presence of phenylhydrazine acetate, and this appears to be the case. At all events, the evidence in support of this view is very strong, and in the light of our recent experiments we must withdraw our previous suggestion that a hexatriose is one of the products of the action of diastase on starch. We cannot at present say if the dextrin and glucose combine together to form a hexatriose thus

$$C_6H_{12}O_6 + C_{12}H_{20}O_{10} = C_{18}H_{32}O_{16},$$

but experiments are in progress to ascertain this.

A mixture of the "isomaltose" (5 grams) prepared by means of diastase from low-dried malt, and glucose (2 grams) was heated with phenylhydrazine acetate in the usual manner. The product was a mixture of glucosazone and a soluble osazone. The latter, after recrystallisation, melted at 150—160°, and gave the following result on analysis.

0·1568 gave 13·5 of moist nitrogen at 21·5° and 757·4 mm. N = 9·73.*
The formula $C_{18}H_{30}O_{14}(N_2HC_6H_5)_2$ requires N = 8·21 per cent.;
whilst $C_{12}H_{20}O_{10}(N_2HC_6H_5)_2$ requires N = 10·76 per cent.

The values therefore indicate that the substance is a mixture of a hexatriosazone and a hexabiosazone, a result which was to be expected seeing that maltose is a constituent of the "isomaltose." A thorough microscopical examination of this osazone showed that it consisted almost entirely of the spherical aggregates of needles, but the presence of flat, ribbon-like crystals could be distinctly made out under a higher power. We have frequently observed that when the hexatriosazone is associated with maltosazone a coating of crystals adheres to the sides of the vessel in which it has been crystallised, and this was so in the case of the osazone now under discussion. On the other hand, the pure triosazone can be poured on to a filter from the vessel in which it has been crystallised without leaving any of the substance adhering to the sides of the latter.

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* We are indebted to Mr. F. W. Streatfeild for this determination.

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LXXVII.—*Transformation of Ammonium Cyanate into Urea.*

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Since Wöhler's memorable observation that ammonium cyanate spontaneously undergoes transformation into urea, the subject, probably from the very magnitude of the result achieved, has been entirely neglected. One or two points of interest, however, occur in connection with this transformation, and it is the object of the present paper to draw attention to them.

Liebig and Wöhler (*Ann. Phys. Chem.*, 1830, **20**, 393) note that whilst the change takes place immediately on boiling the aqueous cyanate solution, it is gradual when the solution is left to evaporate in the air, or is evaporated by the aid of a gentle heat. It thus seemed possible that the course of the reaction might be followed at different temperatures, provided that a method could be found for estimating in a simple fashion the amount of ammonium cyanate or of urea in the solution at any specified time. Such a method was developed by taking advantage of the circumstance that silver nitrate has no action on urea, whereas with ammonium cyanate it yields a silver salt practically insoluble in cold water.

Method of Estimation.

The mode of experiment was as follows. A measured volume of the solution to be investigated was introduced into a small flask containing a known volume of decinormal silver nitrate solution, in excess of the quantity necessary to completely precipitate the cyanate. The contents of the flask were cooled as rapidly as possible to the ordinary temperature by means of a stream of water, and allowed to remain for a few minutes. The silver cyanate had then, as a rule, collected to an easily-filtered precipitate, the filtrate from it being either quite clear or only slightly opalescent. The contents of the flask were thrown on a 5-cm. filter, the flask rinsed out twice with water, and the precipitate washed three times on the filter. The filtrate was then transferred to a porcelain basin, and the excess of silver in it titrated by Volhard's method with 1/50 N ammonium thiocyanate solution.

The solubility of silver cyanate in water at the ordinary temperature is so slight as to be within the experimental error of the method. It was found that the amount dissolved by 100 parts of water at 16° is 0·006; that is, 25 c.c. of water dissolve what corresponds to 0·1 c.c. of 1/50 N thiocyanate solution. As the filtered solution, including wash water, never amounted to more than 50 c.c., the maximum error from this source is 0·2 c.c. of thiocyanate solution; and this amount is never even approximately reached, as the solubility of silver cyanate is greatly diminished by the presence of the silver nitrate in the filtrate. An experiment with centinormal silver nitrate, instead of water, showed that the solubility of silver cyanate in this solvent is so small as not to be detected in the titration.

The error of the method, that is, in the filtration, washing, and titration, may be estimated at 0·1 c.c. of the thiocyanate solution, two determinations with the same sample seldom differing by more than that amount.

Reversibility of the Transformation.

It seems to have hitherto escaped observation, that urea, when heated at 100° with water, is partially retransformed into ammonium cyanate. It is of course well known that silver cyanate is formed when a solution of urea is evaporated down with silver nitrate, but this has been uniformly attributed to a specific action of the silver salt. Urea itself gives no precipitate with silver nitrate, but if a solution of it be kept at 100° for half an hour, then cooled and a silver salt added, it gives a considerable precipitate, which has the characteristic properties of silver cyanate. That this precipitate is formed by the double decomposition of silver nitrate with ammonium cyanate is proved by the fact that the quantity of silver cyanate obtained keeps equal pace with the amount of ammonia found in the solution by Nessler's process. Thus a decinormal solution of urea, which originally gave no coloration with Nessler's solution, yielded the following numbers when heated to 100°. After 10 minutes, the amount of urea transformed, as estimated by the silver nitrate method, was 1·2 per cent., as estimated by Nessler's method 1·3 per cent. After 25 minutes the corresponding numbers were 3·2 per cent. and 4 0 per cent. respectively. These numbers agree with each other within the experimental error, as the quantities estimated were very small.

Preparation of Ammonium Cyanate Solutions.

The method adopted for the preparation of the solutions of ammonium cyanate was the decomposition of silver cyanate by ammonium chloride. The silver cyanate was prepared by heating a seminormal solution of silver nitrate with 5 equivalents of urea for four hours at 100°, the silver cyanate produced being filtered off twice or thrice in that interval. The silver salt obtained in this way was in the form of fine needles, and required no purification. It was drained on a filter plate, washed thoroughly with water, and dried in an exhausted desiccator. The yield, with the quantities given above, is 88 per cent. of the silver nitrate taken, in accordance with the theoretical number of 90 per cent., the mode of deducing which will be given later.

0·4995 silver cyanate gave 0·3585 Ag. Ag = 71·8. Calculated Ag = 72·0 per cent.

The ammonium cyanate solution for each day's work was prepared specially, as even at the ordinary temperature the transformation into urea is fairly rapid. To obtain the solution of the requisite strength, a weighed quantity of finely powdered silver cyanate, very slightly in excess of that calculated, was washed into a measuring flask, into which had been introduced a quantity of ammonium chloride, accurately weighed to give the ammonium cyanate solution of the proper strength when the mixture was diluted to the mark. Occasionally a measured quantity of ammonium chloride solution of known concentration was added instead of the weighed solid. After the flask had been filled to the mark with water, the contents were kept continually agitated for an hour, as the action between the practically insoluble silver cyanate and the ammonium chloride is comparatively sluggish. At the end of that time, however, it may be assumed to be complete, for a part of the filtered solution when treated with nitric acid gives no precipitate, either with silver nitrate or with ammonium chloride. Each filtered solution was tested in this way before being used, and rejected if more than a slight opalescence appeared with either of the reagents.

Determination of the Equilibrium Point.

For the calculation of the velocity constant of the reaction, it was necessary to determine the point at which the transformation ceased. This point should be the same, whether approached from the ammonium cyanate end or from the urea end, as it is the point at which the two opposed actions are balanced, as much ammonium cyanate being transformed into urea in a given time as is reproduced from the urea in the same time. As the rate at which the ammonium cyanate is converted into urea is much greater than the rate of the reverse action, it follows that the end-point must lie near the urea end.

Experiments with decinormal urea at 100° gave the following results.

t.	Titre.	Percentage of urea transformed.
0	5·00	0
14	4·40	2·4
60	3·85	4·6
120	3·90	4·4
182	3·90	4·4
0	5·00	0
15	4·60	1·6
32	4·10	3·6
55	3·90	4·4
87	3·95	4·2
107	3·90	4·4

In the first column, the time in minutes from the beginning of the heating is given. In the second column, we have the numbers obtained by adding 5 c.c. of the solution to 1 c.c. of decinormal silver nitrate, filtering, and titrating with 1/50 N ammonium thiocyanate solution. Four times the difference between these numbers and 5·0 gives the percentage of urea transformed. It is apparent that after an hour the end-point is reached, no further change in the titre taking place.

Approaching the end-point from the other side (decinormal ammonium cyanate) we obtained the following results.

t.	Titre.	Percentage of cyanate transformed.
0	0	0
11	18·9	75·6
30	20·9	83·6
60	21·3	85·2
90	22·3	89·2
120	23·2	92·8

Five c.c of the solution were added to 5 c.c. of decinormal silver nitrate, and the filtrate titrated as usual with 1/50 N thiocyanate. The quantity of urea transformed in no case that we observed exceeded 93 per cent., the maximum numbers obtained in a considerable number of experiments averaging 91 6 per cent. This number, when added to the number obtained from the urea experiment, should give a sum equal to 100, but, as we see, the sum on the average only reaches 96. This deficit, however, is easily accounted for. Ammonium cyanate, while passing for the most part into urea, undergoes at the same time a subsidiary transformation into ammonium carbonate. Now, 1 mol. of ammonium cyanate is transformed into 1 mol. of ammonium carbonate, but whilst the former fixes one equivalent of silver nitrate, the latter fixes two; so that more silver nitrate is precipitated than would be the case if no such secondary transformation had occurred, and the quantity of silver left for titration in the filtrate is in consequence too small. The formation of ammonium carbonate can be detected by the solution giving a precipitate with calcium nitrate, this precipitate dissolving with effervescence in acetic acid. A quantitative experiment gave the following results.

Forty c.c. of a decinormal ammonium cyanate solution, which had undergone transformation at 69°, were precipitated with calcium nitrate and a little ammonia. The carbonate obtained was converted into calcium sulphate, the weight of which was found to be 0·0221 gram. This corresponds to 10 milligrams of ammonium cyanate, the total quantity in 40 c.c. of a decinormal solution being 0·24 gram. Thus 4 per cent. of the ammonium cyanate had been converted into ammonium carbonate, an amount which exactly accounts for the deficit above noted.

It will be seen from the table that the conversion of ammonium cyanate into urea at 100° proceeds very rapidly, three-fourths of the total amount being transformed in 11 minutes. In every case, a brown turbidity was observed in the solution after 30 minutes at 100°, which was probably due to the reduction of a trace of silver compound in the solution. The silver precipitates, also, obtained from solutions at this temperature, were usually brown, marking a secondary decomposition of the ammonium cyanate.

The true end-point for the equilibrium between ammonium cyanate and urea must lie very close to that obtained with urea solutions, for there the amount of ammonium cyanate, and consequently the amount of secondary decomposition, is throughout at a minimum. No appreciable precipitate with calcium nitrate was obtained with such solutions, and we may thus assume that the theoretical end-point of the transformation of ammonium cyanate into urea, were there no secondary decomposition, would, at 100°, lie at 95 per cent. with a possible error of 0·5 per cent.

It was of both theoretical and practical importance to determine the displacement of the end-point by variation of temperature, and experiments were made with this object.

At low temperatures, the transformation of urea proceeds so slowly that the end-point might only be reached after weeks or even months. Solutions were therefore made up containing both urea and ammonium cyanate in such proportions that the composition approximated to that of the solution in equilibrium at 100°. A decinormal solution with 5 per cent. of cyanate and 95 per cent. of urea did not change in titre on remaining for 43 hours at 39°. A similar solution, containing 2 per cent. of cyanate and 98 per cent. of urea, showed a diminution of 0·25 c.c., or 0·5 per cent. under the same conditions. Some of the urea had therefore been converted into ammonium cyanate, so that we must conclude that temperature influences the end-point but little, since at 100° it stands at 95 per cent., and at 39° lies between that figure and 97·5 per cent. at the utmost, being, in all probability, much nearer the former than the latter.

As the velocity experiments were all made with ammonium cyanate solutions, the "practical" end-point, as recorded by the maximum titre at 100°, was taken instead of the real end-point, which does not allow for the secondary decomposition of the cyanate. Thus, with decinormal solutions, the calculations were performed with the end-point 91·6 per cent., or 22·9 c.c. of the titrating solution, except in the case of the experiments at 25° and 39°, where the secondary decomposition, as judged by the amount of precipitate with calcium nitrate, was much smaller. For these temperatures, the end-points 94 and 92·8 were taken, but the value of the velocity constant is thereby very little affected.

Calculation of the Velocity Constant.

The decinormal solution of ammonium cyanate was heated to the temperature of observation as soon as possible after its preparation. As will be seen later, its rate of transformation rises very rapidly with the temperature, so that in order to get a zero-time from which the intervals could be calculated, the heating had to be quickly performed. The solution, usually about 70 c.c., was placed in a 4-oz. flask and heated with the naked flame to the temperature of the thermostat in which it was to be placed. This process occupied little more than a minute at most, so that the error in calculating the time is comparatively small, even at the higher temperatures, and the influence of initial disturbances slight. At suitable intervals, 5 c.c. of the solution were removed from the well-corked flask, added to 5 c.c. of decinormal silver solution, cooled, filtered, and titrated.

The following numbers were obtained at 50·1°. In the table, *t* indicates the interval in minutes from the time at which the solution acquired the temperature of observation, x is the titre, and A the end-point, expressed in c.c. of the 1/50 N thiocyanate solution.

Decinormal Cyanate at 50·1°. $A = 22·9$.

t.	x.	$A - x$.	$\frac{1}{t} \log \frac{A}{A - x}$.	$\frac{1}{t} \cdot \frac{x}{A - x}$.
45	4·4	18·5	0·00206	0·00528
72	6·5	16·4	0·00201	0·00549
107	8·3	14·6	0·00183	0·00529
157	10·1	12·8	0·00161	0·00502
230	12·3	10·6	0·00145	0·00505
312	14·2	8·7	0·00134	0·00524
600	17·2	5·7	0·00101	0·00502

Before Guldberg and Waage had formulated and applied in all directions the law of mass action, it had been shown by Wilhelmy and by Harcourt and Esson that when one molecule was transformed into another or others, the rate at which this transformation occurred was expressed by a logarithmic formula, which is deduced from the general law as follows. Let A be the original active mass of the substance undergoing transformation, and let x have been transformed at the time t, then the rate of transformation, $\frac{dx}{dt}$, at that time will be

$$\frac{dx}{dt} = C(A - x),$$

that is, proportional to the active mass, $A - x$, of the substance then untransformed. The constant, C, is the velocity constant of the reaction. Bearing in mind that when $t = 0$, $x = 0$, we obtain, on integration,

$$\log_e \frac{A}{A - x} = Ct;$$

or, if we use the decadic instead of the natural logarithms,

$$\frac{1}{t} \log \frac{A}{A - x} = 0·4343\ C.$$

Now both magnitudes on the right hand side of the equation are constant, therefore if the action is a simple transformation of 1 mol. of ammonium cyanate into 1 mol. of urea, the expression $\frac{1}{t} \log \frac{A}{A - x}$ should be constant. A glance at the table shows that this expression, instead of being constant, sinks steadily to half its original value. It is true that instead of the real active mass of the cyanate at the beginning of the action, namely, 25 c.c. in our arbitrary units, we have employed the number 22·9, the practical end-point. But it is capable of a simple mathematical proof that in a unimolecular reversible reaction this mode of procedure is permissible, the logarithmic expression given above being constant as well as the more complicated expression which involves the real active mass and takes account of the opposed reaction, that is, the simultaneous transformation of urea into ammonium cyanate.

We are thus forced to conclude that the production of urea from ammonium cyanate does not proceed in so simple a way as we might be disposed to imagine.

Let us now proceed on the assumption that the interaction of two molecules is necessary for the production of urea. If, as before, we represent the active mass of each kind of molecule (supposed to be present in equivalent quantities) by A, and the quantity transformed at the time t by x, we have, for the rate of transformation,

$$\frac{dx}{dt} = C(A - x)(A - x),$$

this rate being proportional to the active mass of each kind of molecule. The expression obtained on integration is $\frac{x}{A - x} = ACt$, or $\frac{1}{t} \cdot \frac{x}{A - x} = AC$, a constant quantity.

Neglecting, as in the previous case, the slow reverse action by taking the value of the practical end-point as the original active mass, we find that the expression $\frac{1}{t} \cdot \frac{x}{A - x}$ is now indeed constant. Reference to the table will show that the constancy is not absolute, but, from beginning to end, the constant fluctuates about the mean value, exhibiting no steady increase or decrease like the logarithmic expression. The maximum variation from the mean is only 6 per cent., and this will be deemed satisfactory when we consider that one-tenth of a degree difference in temperature causes a variation of 1·5 per cent. Here, then, is distinct evidence that for the production of urea the interaction of two molecules is necessary, and that these must always be present in the ammonium cyanate solution in equivalent proportions. The first assumption to make is that the two molecules are two molecules of ammonium cyanate, but it will be proved in the sequel that this assumption is erroneous. In the meantime, we proceed to give the results of experiments performed at different temperatures in order to ascertain he temperature-coefficient of the expression $\frac{1}{t} \cdot \frac{x}{A - x}$.

Temperature Experiments.

The thermostat employed was a water-bath with windmill and stirrer as described by Ostwald, *Physico-chemical Measurements*, p. 64, and a vapour-pressure thermo-regulator (Benoit's modification of Andreae's, *loc. cit.*, p. 59). The liquids used for filling the various regulators were ether, acetone, methylic alcohol, and ethylic alcohol.

The results obtained are exhibited in the following tables, the symbols being as before.

Decinormal Cyanate at 25·0°. $A = 23·5$.

t.	x.	$A - x$.	$\frac{1}{t} \cdot \frac{x}{A - x}$.
1325	5·6	17·9	0·000236
1970	7·0	16·5	0·000214
2725	9·0	14·5	0·000228
5640	13·3	10·2	0·000231
		Mean =	0·000227

Decinormal Cyanate at 39·0°. $A = 23·2$.

t.	x.	$A - x$.	$\frac{1}{t} \cdot \frac{x}{A - x}$.
228	6·1	17·1	0·00156
373	8·2	15·0	0·00147
591	9·9	13·3	0·00126
1266	14·6	8·6	0·00134
1577	16·1	7·1	0·00143
		Mean =	0·00141

Decinormal Cyanate at 59·7°. $A = 22·9$.

t.	x.	$A - x$.	$\frac{1}{t} \cdot \frac{x}{A - x}$.
15	4·3	18·6	0·0154
30	6·7	16·2	0·0138
50	9·5	13·4	0·0142
80	12·1	10·8	0·0140
140	15·4	7·5	0·0147
		Mean =	0·0144

Decinormal Cyanate at 64·5°. $A = 22·9$.

t.	x.	$A - x$.	$\frac{1}{t} \cdot \frac{x}{A - x}$.
20	7·0	15·9	0·0220
37	10·3	12·6	0·0221
50	12·1	10·8	0·0224
65	13·8	9·1	0·0233
95	16·0	6·9	0·0244
150	17·7	5·2	0·0227

Mean = 0·0228

Decinormal Cyanate at 69·2°. $A = 22·9$.

t.	x.	$A - x$.	$\frac{1}{t} \cdot \frac{x}{A - x}$.
10	6·7	16·2	0·041
15	8·7	14·2	0·041
20	9·9	13·0	0·038
30	12·2	10·7	0·038
45	15·0	7·9	0·042

Mean = 0·040

Decinormal Cyanate at 74·7°. $A = 22·9$.

t.	x.	$A - x$.	$\frac{1}{t} \cdot \frac{x}{A - x}$.
15·5	11·3	11·6	0·063
37·0	15·7	7·2	0·059
60·0	17·9	5·0	0·060
124·0	20·4	2·5	0·066

Mean = 0·062

Decinormal Cyanate at 75·0°. $A = 22·9$.

t.	x.	$A - x$.	$\frac{1}{t} \cdot \frac{x}{A - x}$.
12	9·7	13·2	0·061
27	14·7	8·2	0·066
45	17·0	5·9	0·064
65	18·3	4·6	0·061

Mean = 0·063

Decinormal Cyanate at 80·0°. $A = 22·9$.

t.	x.	$A - x$.	$\frac{1}{t} \cdot \frac{x}{A - x}$.
14	13·3	9·6	0·099
26	16·3	6·6	0·095
44	18·5	4·4	0·096
64	20·1	2·8	0·112
		Mean =	0·100

Decinormal Cyanate at 80·1°. $A = 22·9$.

t.	x.	$A - x$.	$\frac{1}{t} \cdot \frac{x}{A - x}$.
7	9·0	13·9	0·093
17	14·6	8·3	0·103
37	17·9	5·0	0·097
57	19·5	3·4	0·101
97	20·9	2·0	0·108
		Mean =	0·100

These numbers will suffice to show that the expression $\frac{1}{t} \cdot \frac{x}{A - x}$ remains substantially constant at each of the temperatures studied. The determinations at the higher temperatures are difficult on account of the rapidity of the transformation. In the case of the two highest, duplicate experiments are given, which show that although the individual values vary considerably, the mean is sensibly the same.

The temperature, as is usual in such cases, has an enormous influence on the rate of the action. Whilst at 80° half of the ammonium cyanate has been transformed in 10 or 12 minutes, at 25° three days are required to produce the same effect.

Van't Hoff (*Etudes*, p. 114) and Arrhenius (*Zeit. physikal. Chem.*, 4, 227) have shown that the formula

$$C_1 = C_0 e^{A(T_1 - T_0)/T_0T_1}$$

is capable of representing the influence of temperature on a velocity constant with great accuracy, and have endeavoured to assign its theoretical significance. In the expression, C_0 is the velocity constant at the temperature t_0, C_1 the constant at t_1; e is the base of the natural logarithms, T_0 and T_1 are the temperatures t_0 and t_1 when measured in the absolute scale; A, finally, is a numerical constant. Using this formula, and taking the lowest temperature as t_0, we obtain the following table.

$t_0 = 25°$, $C_0 = 0·000227$, $A = 11700$.

t.	C (obs.).	C (calc.).
25·0	0·000227	(0·000227)
39·0	0·00141	0·00133
50·1	0·00520	0·00480
59·7	0·0144	0·0137
64·5	0·0228	0·0227
69·2	0·040	0·0365
74·7	0·062	0·0623
80·0	0·100	0·105

In view of the fact that in the range examined, the constant increases more than four hundred fold, the accordance between the calculated and observed numbers may be looked upon as satisfactory.

Influence of Dilution.

In unimolecular reactions, the concentration of the substance which is being transformed has no effect on the course of the action. If at a certain temperature and a certain concentration half of the substance has undergone transformation in a certain time, the same time will be occupied in producing the half-transformation whether we dilute the original solution, or whether we concentrate it. The velocity constant is here independent of the degree of dilution. This is easily comprehensible from the mechanical point of view, for each molecule is transformed independently of all the rest, so that it is a matter of indifference whether the individual molecules of the substance are closely packed together, or not. The case is different in a bimolecular reaction. Here two molecules must meet before transformation can take place, and their chances of meeting are reduced as we dilute the solution, so that the proportion transformed in a given time will be less the more dilute the solution becomes. The effect on the expression $\frac{1}{t} \cdot \frac{x}{A-x}$, will be seen on reference to the integrated equation

$$\frac{1}{t} \cdot \frac{x}{A - x} = AC.$$

If we reduce the value of A to one-half by halving the concentration, the right-hand side of the equation is halved, for C is a constant independent of the dilution, being in fact the rate at which the action progresses when the reacting substances are present (and maintained) at *unit* concentration. The left-hand side of the equation must also therefore be halved, so that by taking twentieth-normal ammonium cyanate, the expression $\frac{1}{t} \cdot \frac{x}{A-x}$ should be reduced to one-half its value for a decinormal solution. It will be observed that in calculating this expression, any unit may be used for A and x, since we are only concerned with the ratio $x/(A-x)$.

0·05-*normal Cyanate at* 49·8°. $A = 22·9$.

t.	x.	$A - x$.	$\frac{1}{t}\cdot\frac{x}{A-x}$.
120	6·0	16·9	0·00282
180	7·8	15·1	0·00287
240	9·5	13·4	0·00295
400	12·4	10·5	0·00295
533	13·9	9·0	0·00288

Mean = 0·00289

The value of the constant at 50·1° for the decinormal solution is 0·00520. If we double 0·00289, we obtain 0·00578, which is greater than the theoretical value, and is further augmented by applying the correction for the difference in temperature.

0·2-*normal Cyanate at* 60·1°. $A = 22·5$.

t.	x.	$A - x$.	$\frac{1}{t}\cdot\frac{x}{A-x}$.
10·0	4·65	17·85	0·0260
25·0	8·6	13·9	0·0247
40·3	11·3	11·2	0·0252
60·0	13·8	8·7	0·0264
127·0	17·2	5·3	0·0256

Mean = 0·0255

The end-point 22·5 was determined by a special experiment.

0·05-*normal Cyanate at* 60·1°. $A = 22·9$.

t.	x.	$A - x$.	$\frac{1}{t}\cdot\frac{x}{A-x}$.
28	4·4	18·5	0·0085
50	6·8	16·1	0·0085
76	9·0	13·9	0·0085
120	10·8	12·1	0·0074
200	14·2	8·7	0·0082

Mean = 0·0082

We have thus the series

	0·05	0·1	0·2-normal.
Const.	0·0082	0·0144	0·0255

Here the fifth-normal solution which should have a constant four times as great as the twentieth-normal solution has in fact a constant only little more than three times as great. The transformation, then, although it preserves the characteristic constant of a bimolecular reaction at various dilutions, is influenced in some secondary way by the dilution, the tendency being to give too great a constant as the dilution is increased. An explanation of this secondary action will be given in the next section.

Influence of Neutral Salts.

We have now to consider the reason why the transformation of ammonium cyanate into urea is a bimolecular reaction, and not a unimolecular reaction as might *à priori* be expected. The two reacting substances must be present in the ammonium cyanate solution in equivalent proportions, otherwise the expression $\frac{1}{t} \cdot \frac{x}{A-x}$, would not remain constant. The assumptions which might account for this are, 1st, that two molecules of ammonium cyanate meet to form urea; 2nd, that the ammonium cyanate is dissociated by the water wholly or largely into ammonia and cyanic acid, and 3rd, that the ammonium cyanate is electrolytically dissociated into ammonium ions and cyanic ions. A means of ascertaining which of these assumptions is correct is to be found in the influence exercised by various substances on the constant. A perfectly indifferent salt has in general little influence; it may slightly alter the numerical value of the constant but no more. The following experiment was made with potassium sulphate added in equivalent proportion to the solution of ammonium cyanate.

Decinormal Ammonium Cyanate in Presence of Decinormal Potassium Sulphate at 74·7°. $A = 22·0$ by experiment.

t.	x.	$A - x$.	$\frac{1}{t} \cdot \frac{x}{A-x}$.
9	7·4	14·6	0·056
23	12·7	9·3	0·059
47	16·0	6·0	0·057
70	17·3	4·7	0·053
103	18·7	3·3	0·055
		Mean =	0·056

The effect of the potassium sulphate is to reduce the constant from 0·062 to 0·056. This might well be in accordance with any of the above assumptions, the influence being comparatively slight. On the third assumption, a slight diminution of the constant might be predicted, for the number of active molecules, that is NH_4 and CNO, is diminished by the addition of another salt. If, instead of potassium sulphate, we add an equivalent of ammonium sulphate the effect is wholly different. The action is greatly accelerated and the expression $\frac{1}{t} \cdot \frac{x}{A-x}$ is no longer constant, increasing rapidly, especially towards the end of the reaction.

Decinormal Ammonium Cyanate in Presence of Decinormal Ammonium Sulphate at 74·7°. A = 24·7 by experiment.

t.	x.	$A-x$.	$\frac{1}{t} \cdot \frac{x}{A-x}$.
8	10·8	13·9	0·097
20	17·5	7·2	0·122
40	21·9	2·8	0·195

Here in 10 minutes the transformation has proceeded half way. In presence of potassium sulphate nearly 20 minutes elapse before the solution has reached the same condition. It will be seen too that the end-point practically corresponds to complete transformation into urea. This is a natural result of the great acceleration of the forward action towards the end, the reverse transformation remaining constant. The lowest value of $\frac{1}{t} \cdot \frac{x}{A-x}$ is 50 per cent. greater than the value 0·062 for ammonium cyanate alone, and the highest one 200 per cent. The acceleration is, therefore, of quite a different order from the influence exerted by potassium sulphate.

The only reasonable explanation of this acceleration is that the quantity of one or more of the active substances present has been largely increased by the addition of ammonium sulphate. On the first assumption that the active substances are ammonium cyanate molecules, this increase is impossible, so this assumption may be dropped. Unless we assume that ammonium sulphate is to a great extent dissociated into ammonia and sulphuric acid when dissolved in water, an assumption which few will grant, the second supposition must also be set aside: independent evidence of its inadequacy will be given later. There remains then the third assumption that the reacting molecules are ammonium ions, NH_4, and cyanic ions, CNO, produced by the electrolytic dissociation of the ammonium cyanate. On the dissociation hypothesis, ammonium sulphate is also decomposed electrolytically when dissolved in water, the ions being NH_4 and SO_4. On adding ammonium sulphate to the solution, then, we increase the active mass of one of the reacting substances, namely the ammonium ion, and consequently the action proceeds faster, especially towards the end, for then the added ammonium ions bear a greater proportion to the total than they do at the beginning. The experimental result is thus in harmony with the theory of electrolytic dissociation.

An increase in the quantity of the other reacting substance, the cyanic ion, ought also to have an accelerating effect on the action. According to the dissociation theory, potassium cyanate like other potassium salts of monobasic acids, is almost completely dissociated into its ions K and CNO in dilute aqueous solution, so the addition of potassium cyanate should hasten the action considerably. This we find to be the case.

Decinormal Ammonium Cyanate in Presence of Decinormal Potassium Cyanate at 74·7°.

t.	x.
10	13·2
20	16·8
35	20·2
50	21·2
70	21·8

The accelerating effect is of the same order as in the case of the addition of ammonium sulphate. Unfortunately a direct comparison and calculation of the "constant," is impossible, owing to the comparatively great decomposition of cyanate into carbonate which takes place simultaneously with the transformation into urea. After the solution had been heated for an hour, it gave a dense precipitate with calcium nitrate.

As the action at 75° proceeded too rapidly in presence of accelerating agents for accurate calculations, some experiments were performed at 50° in order to obtain more trustworthy data.

When the reacting substances are not present in the solution in equivalent proportion, the expression $\frac{1}{t}\cdot\frac{x}{A-x}$ no longer remains constant and another must be substituted for it. Let the original concentration of the one substance be A, and of the other B, then the rate at any time is expressed by the equation

$$\frac{dx}{dt} = C(A - x)(B - x),$$

which, on integration, becomes

$$\frac{1}{t}\log\frac{(A - x)B}{(B - x)A} = 0·4343\,(A - B)C.$$

All the magnitudes on the right hand side of the equation are constant, so that the left hand side must also be constant. On adding ammonium sulphate in equivalent proportion to a solution of ammonium cyanate, we do not double the number of ammonium ions in the solution, for the sulphate, according to the electrical conductivity, is less dissociated than the cyanate, and each diminishes the dissociation of the other from the value it would have were it dissolved separately in the same volume of water as is used to dissolve both. Using the conductivity numbers of Kohlrausch and others, we find that the ammonium ions in the mixed solution should be to those in the pure cyanate solution in the ratio of 5 : 3 approximately, the number of cyanic ions being very slightly diminished. Taking A for the cyanic ions equal to its former value, we have approximately B for the ammonium ions equal to 1·61 A. Substituting this value for B in the above equation and re-arranging, we obtain

$$\frac{1}{t}\log\frac{A-0{\cdot}62x}{A-x} = 0{\cdot}61 \times 0{\cdot}4343\,C,$$

C having the same numerical value as it had when the ammonium cyanate was alone in the solution.

Decinormal Ammonium Cyanate in presence of Decinormal Ammonium Sulphate at 49·8°.

t.	x.	$A - x$.	$A - 0{\cdot}62x$.	$\frac{1}{t}\log\frac{A-0{\cdot}62x}{A-x}$.
33	5·4	19·3	21·3	0·00129
62	8·0	16·7	19·8	0·00119
99	10·6	14·1	18·1	0·00110
162	14·2	10·5	16·0	0·00117
226	16·6	8·1	14·4	0·00110
			Mean =	0·00117

The value of $A = 24{\cdot}7$ was obtained by direct experiment. It will be seen that the constant is fairly good, and from it we can calculate C by means of the equation

$$0{\cdot}00117 = 0{\cdot}61 \times 0{\cdot}4343\,C.$$

This gives us $C = 0{\cdot}00443$, and when we allow for 0·3° difference in temperature at 15 per cent. per degree, we obtain 0·00463, which is a fair approximation to the value of $C = 0{\cdot}0052$ in the pure cyanate solution at 50·1°.

An experiment was made with a solution decinormal with respect to ammonium cyanate, and 1/20 N. with respect to the ammonium sulphate. Here the amount of ammonium ions is not increased by one-half, but only by a quarter, as a consideration of the conductivities will show, the chief diminution being due to the effect of the cyanate on the less dissociated sulphate. We have therefore $B = 1·25\ A$, and the formula becomes

$$\frac{1}{t}\log\frac{A - 0·8x}{A - x} = 0·25 \times 0·4343\ C.$$

For A we have the value 24·4 determined by an end-point experiment.

Decinormal Ammonium Cyanate in presence of 0·05-*normal Ammonium Sulphate at* 49·9°.

t.	x.	$A - x$.	$A - 0·8x$.	$\frac{1}{t}\log\frac{A - 0·8x}{A - x}$.
43	5·2	19·2	20·2	0·00051
71	7·8	16·6	18·2	0·00056
113	9·9	14·5	16·5	0·00050
170	12·4	12·0	14·5	0·00048
235	14·6	9·8	12·7	0·00048
395	18·4	6·0	9·7	0·00053
			Mean =	0·00051

From the mean 0·00051 we obtain C by the equation

$$0·00051 = 0·4343 \times 0·25\ C.$$

This gives us $C = 0·0047$, from which, if we add 3 per cent. as the temperature correction, we get the value $C = 0·00484$ for the constant at 50·1°, in close approximation to the observed value, 0·0052.

Considering the slight uncertainty that attaches to the calculation of the exact degree of dissociation from the conductivities as tabulated in Ostwald's *Lehrbuch*, vol. II, pt. 1, the constancy of these numbers and the values they give for C must be held as strong evidence in favour of the application of the dissociation theory to the matter in hand.

In the last section, it was found that the influence of dilution on the speed of the action was disturbed by some secondary action, which, at low concentrations, tended to give a greater constant than theory predicted. If we take the degree of dissociation at the various dilutions into account, however, the discrepancy disappears. At low concentrations, the degree of dissociation, as indicated by the conductivities, is greater than at higher concentrations, so that in the more dilute solutions there are relatively more of the active ions than in the more concentrated solutions. At the dilution $\frac{1}{4}$ N., the value of $\frac{1}{t}\cdot\frac{x}{A - x}$ was found to be 0·0255; at the dilution $\frac{1}{30}$ N., it was 0·0082. If there were four times as many ions at the dilution $\frac{1}{5}$ N. as at $\frac{1}{20}$ N., the value for the former should be 0·0328 instead of 0·0255; but the conductivities show that there are only 3·3 times as many ions, so we obtain 0·0082 × 3·3 = 0·0270, not far removed from the observed value, 0·0255.

To apply a final test to the validity of the theory of electrolytic dissociation in this connection, an experiment was made with ammonium cyanate in presence of ammonia. If the dissociation caused by the water is a dissociation into ammonia and cyanic acid, and into ammonia and sulphuric acid, we should have ammonia solution producing at least the same effect as an equivalent solution of ammonium sulphate. On the other hand, if we consider the conductivities of ammonia solutions, the dissociation theory predicts that ammonia should behave towards ammonium cyanate as an indifferent substance like potassium sulphate. The conductivities obtained by Bredig (*Zeit. physikal. Chem.*, 1894, **13**, 294) show that in decinormal solution, ammonia is dissociated only to the extent of 1·5 per cent. into its ions. This amount of dissociation is diminished to the vanishing point in presence of the highly dissociated ammonium cyanate, so that as the ammonia contributes no ammonium ions to the solution, it will behave as an indifferent substance. The following are the results obtained.

Decinormal Ammonium Cyanate in Presence of Decinormal Ammonia at 49·4°. A = 22·9.

t.	x.	$A - x$.	$\frac{1}{t} \cdot \frac{x}{A - x}$.
71	5·6	17·3	0·00456
110	7·4	15·5	0·00434
155	9·2	13·7	0·00433
215	11·2	11·7	0·00445
		Mean =	0·00442

In performing this experiment, the silver nitrate into which the measured quantity of solution was poured, was mixed with a quantity of nitric acid exactly sufficient to neutralise the free ammonia, in order that the solubility of the silver cyanate might not be increased. The expression $\frac{1}{t} \cdot \frac{x}{A - x}$ remains constant, as if no active substance had been added, and its value, 0·0049, when corrected for temperature, is very near the value 0·0052, obtained with ammonium cyanate alone at 50·1°. Ammonia then behaves towards ammonium cyanate in precisely the same way as potassium sulphate does, in harmony with the requirements of the dissociation theory.

We find, then, that the consistent application of the theory of electrolytic dissociation accounts for the bimolecular nature of the transformation of ammonium cyanate into urea, the quantitative influence on it of dilution, and of the presence of potassium sulphate, potassium cyanate, ammonium sulphate, and ammonia. On no other theory, as it appears to us, can even a qualitative explanation of our results be given.

Interaction of Urea and Silver Nitrate.

As we have already stated, the silver cyanate used in these experiments was prepared by heating semi-normal silver nitrate solution at 100° with five equivalents of urea. The yield of silver cyanate was in no case greater than 88 per cent. of that theoretically possible, continued heating causing no further precipitation beyond this quantity. The silver cyanate is, of course, produced by the interaction of the silver nitrate and the ammonium cyanate formed from the urea. As the ammonium cyanate is removed from the solution as fast as it is formed, it might, at first sight, be expected that, since a great excess of urea is present, the action would go on until practically all the silver is precipitated, unless the silver cyanate were comparatively soluble in water at 100°. The solubility, however, is not great, 100 c.c. of a saturated aqueous solution of silver cyanate at 100° containing only 0·12 gram of the salt, that is, the solution is 0·008 normal. In the actual solution this solubility is much diminished by the presence of undecomposed silver nitrate, yet it is the minute quantity of silver cyanate dissolved which determines the stoppage of the action at a point so much short of the possible yield.

The point of equilibrium may be easily calculated on the dissociation theory as follows. We found that at 100°, 5 per cent. of a decinormal solution of urea was transformed into ammonium cyanate. Assuming, for simplicity's sake, that the ammonium cyanate is entirely dissociated, which is very nearly the case, we have the following equation to express the equilibrium between the urea and the cyanate.

$$0{\cdot}005 \times 0{\cdot}005 = K \times 0{\cdot}095.$$

The magnitudes on the left-hand side are the active masses of the ammonium and cyanic ions in terms of a normal solution; on the right-hand side K is the ratio of the velocity constants (which remains unaltered so long as the temperature is the same) and 0·095 is the active mass of the urea. From this equation we obtain

$$K = 0{\cdot}000263,$$

which determines the equilibrium between the urea and the ammonium and cyanic ions.

Now, when silver nitrate is added, the cyanic ions can only come from the unprecipitated silver cyanate, so that their number is determined by the solubility of the silver cyanate. According to the theory developed by Nernst, and experimentally verified by him and by Noyes, the solution equilibrium is of such a kind that the concentration of the *undissociated* silver cyanate in solution remains constant. But for the equilibrium between dissociated and undissociated silver cyanate we have the equation

$$\text{Act. mass Ag} \times \text{act. mass CNO} = K' \times \text{act. mass AgCNO}.$$

As K' is a constant, and the active mass, that is, the concentration, of the undissociated silver cyanate remains constant, the right-hand side of the equation is constant, and is very nearly equal to 0·000064; for the concentration of the saturated solution of silver cyanate at 100° is 0·008, and this may be taken as the active mass of each ion, the cyanate being almost entirely dissociated, so that the left-hand side is $0{\cdot}008 \times 0{\cdot}008 = 0{\cdot}000064$. We are now in possession of the two constants which enable us to calculate the equilibrium. The solubility of the silver cyanate determines the number of cyanic ions, which again determines the number of ammonium ions required to produce equilibrium with the urea. But the number of ammonium ions corresponds to the number of silver ions which have disappeared, and this number influences the solubility of the silver cyanate. The problem is, therefore, to find the concentration of cyanic ions which will be in equilibrium on the one hand with the undissociated (and solid) silver cyanate, and on the other with the urea. Let the concentration of the ammonium nitrate in solution at the equilibrium be x-normal, then the concentration of the silver nitrate will be $0{\cdot}5 - x$, and of the urea $2{\cdot}5 - x$. The concentration of the cyanic ions is determined by the last equation to be 0·000064 divided by the concentration of the silver ions. This concentration may be taken as equal to $0{\cdot}5 - x$, as the silver nitrate is nearly all dissociated, and the quantity coming from the silver cyanate in solution is very small. We are justified in making these assumptions, which simplify the treatment greatly, by the results of Noyes (*Zeit. physikal. Chem.*, 1890, 6, 246), who investigated the parallel case of the solubility of silver bromate in presence of silver nitrate. The detailed treatment of the question is given by him at the place cited. The concentration of the cyanic ions is therefore $0{\cdot}000064/(0{\cdot}5 - x)$. For the equilibrium between ammonium cyanate and urea we have, then,

$$\text{Ammonium} \times \text{cyanic ion} = K \times \text{urea}$$
$$x\{0{\cdot}000064/(0{\cdot}5 - x)\} = 0{\cdot}000263\,(2{\cdot}5 - x).$$

Solving this equation, we find $x = 0{\cdot}45$ to be the concentration of the ammonium nitrate in solution at the equilibrium point. This is equivalent to the quantity of silver cyanate formed, so that we have $0{\cdot}45/0{\cdot}5 = 90$ per cent. of the silver nitrate transformed, the yield actually obtained being 88 per cent.

As it might be thought that the agreement between the calculated and the observed numbers is here due to a chance coincidence from balancing of errors, another experiment was made in which the urea was taken in quantity equivalent to the silver nitrate. It had therefore the concentration 0·5. For this we have the equation of equilibrium

$$x\{0{\cdot}000064/(0{\cdot}5 - x)\} = 0{\cdot}000263\,(0{\cdot}5 - x),$$

the only difference being the substitution of 0·5 for 2·5 in the second member of the last equation. Here we find $x = 0{\cdot}25$. That is, when the silver nitrate and urea are both semi-normal in the solution, 50 per cent. of the silver nitrate should be transformed into silver cyanate. The actual experiment was conducted as follows. Silver nitrate (17 grams) and urea (6 grams) were dissolved separately in hot water, filtered, mixed, heated, and stirred to collect a slight brown precipitate, which was filtered off. The clear solution was made up to 200 c.c. and heated at 100° for four hours with a reflux condenser. After cooling, the silver cyanate was collected, drained, washed, dried, and weighed. The weight obtained was 7·27 grams or 48·33 per cent. of the possible quantity, the predicted yield being 7·5 grams or 50 per cent. The agreement is excellent when the loss in weight by washing is considered. The amount transformed, as estimated by titration of an aliquot portion of the filtrate, was 50·3 per cent. No further precipitate was obtained by continued heating of the solution.

We thus see that the theory of electrolytic dissociation not only enables us to understand the simple equilibrium between urea and ammonium cyanate, but also to account for and predict the phenomena when this equilibrium is complicated by the presence of a salt which reacts with one of these substances.

Heat of Transformation.

We have seen that the influence of temperature on the equilibrium point between urea and ammonium cyanate is very slight, and this corresponds to a small heat of transformation. The formula for calculating the thermal effect cannot be applied in strictness, as the data for the end-points at different temperatures are not sufficiently definite, so that we cannot even say with certainty whether the transformation in dilute solution is accompanied by evolution or absorption of heat; most probably there is a slight heat evolution on the conversion of the cyanate into urea.

LXXVIII.—*Ethereal Salts of Ethanetetracarboxylic acid.*

By James Walker, Ph.D., D.Sc., and J. R. Appleyard, University College, Dundee.

When the alkaline salt of a monobasic fatty acid is subjected to electrolysis, the anion, on losing its charge at the positive electrode, decomposes chiefly in two ways, with production of a saturated and of an unsaturated hydrocarbon. Potassium propionate, for example, yields butane and ethylene according to the equations

I. $2\mathrm{CH_3{\cdot}CH_2{\cdot}COO{\cdot}} = \mathrm{CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3} + 2\mathrm{CO_2}$.

II. $2\mathrm{CH_3{\cdot}CH_2{\cdot}COO{\cdot}} = \mathrm{CH_3{\cdot}CH_2{\cdot}COOH} + \mathrm{CH_2{:}CH_2} + \mathrm{CO_2}$.

Crum-Brown and Walker have shown (*Annalen*, 1891, **261**, 107) that the potassium ethylic salts of saturated dibasic acids behave similarly, with production of a saturated diethylic salt and of an unsaturated monethylic salt. Thus ethylic potassium succinate, on electrolysis, produces diethylic adipate, in accordance with the equation

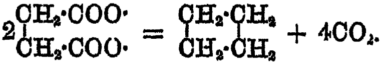
I. $2\mathrm{EtOOC{\cdot}CH_2{\cdot}CH_2{\cdot}COO{\cdot}} = \mathrm{EtOOC{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}COOEt} + \mathrm{CO_2}$.

The equation for the formation of the unsaturated product is

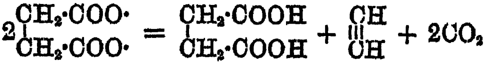
II. $2\mathrm{EtOOC{\cdot}CH_2{\cdot}CH_2{\cdot}COO{\cdot}} = \mathrm{EtOOC{\cdot}CH_2{\cdot}CH_2{\cdot}COOH} + \mathrm{EtOOC{\cdot}CH{:}CH_2} + \mathrm{CO_2}$.

The unsaturated ethylic salt would thus be ethylic acrylate. This product was not actually isolated, but the corresponding ethylic methacrylate was obtained in considerable quantity on electrolysis of ethylic potassium dimethylmalonate.

If the anion of dipotassium succinate decomposed similarly to that of potassium acetate on being discharged at the anode, the products of electrolysis there found would be tetramethylene and acetylene, formed in accordance with the equations

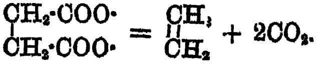
I. 

$$2\begin{array}{l}\mathrm{CH_2{\cdot}COO{\cdot}}\\ \mid\\ \mathrm{CH_2{\cdot}COO{\cdot}}\end{array} = \begin{array}{l}\mathrm{CH_2{\cdot}CH_2}\\ \mid\quad\;\;\mid\\ \mathrm{CH_2{\cdot}CH_2}\end{array} + 4\mathrm{CO_2}.$$

II. 

$$2\begin{array}{l}\mathrm{CH_2{\cdot}COO{\cdot}}\\ \mid\\ \mathrm{CH_2{\cdot}COO{\cdot}}\end{array} = \begin{array}{l}\mathrm{CH_2{\cdot}COOH}\\ \mid\\ \mathrm{CH_2{\cdot}COOH}\end{array} + \begin{array}{l}\mathrm{CH}\\ \equiv\\ \mathrm{CH}\end{array} + 2\mathrm{CO_2}$$

In the case of such a dibasic anion, however, there is a third possibility, for, after the loss of carbonic anhydride, the residual bivalent radicle is capable of independent existence, and thus from dipotassium succinate we may obtain ethylene.

Ia. 

$$\begin{array}{l}\mathrm{CH_2{\cdot}COO{\cdot}}\\ \mid\\ \mathrm{CH_2{\cdot}COO{\cdot}}\end{array} = \begin{array}{l}\mathrm{CH_2}\\ \parallel\\ \mathrm{CH_2}\end{array} + 2\mathrm{CO_2}.$$

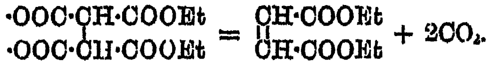
The production of tetramethylene on the electrolysis of a succinate has so far never been observed. Bourgoin states (*Bull. Soc. Chim.*, 1874, **21**, 1695) that when perfectly neutral sodium succinate solution is electrolysed, the gases evolved at the positive electrode are oxygen, carbon monoxide, and carbonic anhydride. Kekulé found, however, that, in presence of a little free alkali, ethylene and acetylene are formed in addition to these products of oxidation, so that two of the three normal decomposition products of the anion have been obtained. The quantity of acetylene produced is inconsiderable.

Since the ethylic potassium salts of dibasic acids behave similarly to the potassium salts of monobasic acids, it might reasonably be expected that the diethylic dipotassium salt of a tetrabasic acid would behave in an analogous manner to the dipotassium salt of a dibasic acid, and, on electrolysis, yield, along with oxidation products, the diethylic salts of an acid with one ethylene linking and of an acid with one acetylene linking. We have endeavoured to ascertain practically if this is the case, the acid chosen for experiment being ethanetetracarboxylic acid. Guthzeit has shown (*Annalen*, 1882, **214**, 72) that the tetrethylic salt of this acid on half saponification yields a diethylic dipotassium salt having the following constitution,

$$COOK\cdot CH(COOEt)\cdot CH(COOEt)\cdot COOK.$$

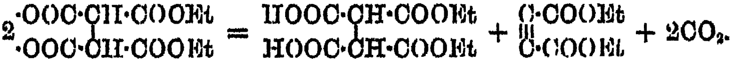
On electrolysis, the anion should decompose as follows.

I*a*.



$$\begin{array}{l}\cdot OOC\cdot CH\cdot COOEt\\ \quad\quad\ \ |\\ \cdot OOC\cdot CH\cdot COOEt\end{array} = \begin{array}{l}CH\cdot COOEt\\ \|\\ CH\cdot COOEt\end{array} + 2CO_2.$$

II.

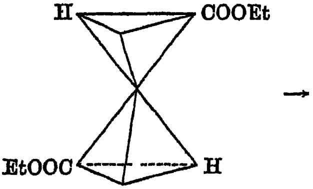


$$2\begin{array}{l}\cdot OOC\cdot CH\cdot COOEt\\ \quad\quad\ \ |\\ \cdot OOC\cdot CH\cdot COOEt\end{array} = \begin{array}{l}HOOC\cdot CH\cdot COOEt\\ \quad\quad\ \ |\\ HOOC\cdot CH\cdot COOEt\end{array} + \begin{array}{l}C\cdot COOEt\\ \|\!|\\ C\cdot COOEt\end{array} + 2CO_2.$$

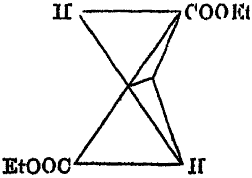
The unsaturated ethylic salt of the first equation has the formula of diethylic maleate or diethylic fumarate, that of the second equation is diethylic ethinedicarboxylate.

The uncertainty as to whether fumaric acid or maleïc acid should be derived from diethylic dipotassium ethanetetracarboxylate arises from this salt having in its molecule two similar asymmetrical carbon atoms, as a glance at the formula shows. The salt therefore ought to exist in an optically inactive, a racemic, and two optically active modifications. Supposing the saponification to take place in such a way that the two optically active modifications were produced in equal proportions, the proximate constituents of the mixture of isomerides would be an inactive racemic salt, and a salt with a really inactive molecule.

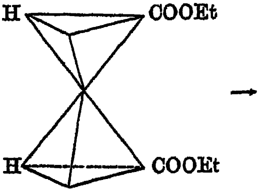
From the optically active salts, that is the racemic salt, diethylic fumarate would be derived on electrolysis; from the optically inactive salt, diethylic maleate. A consideration of the formulæ will make this clear. In the tetrahedra, the blank summits towards the reader are originally occupied by the group ·COOK, which becomes ·COO· in the charged anion, and is blank in the anion after the loss of carbonic anhydride. The unsaturated substance is formed by the two blank summits meeting.



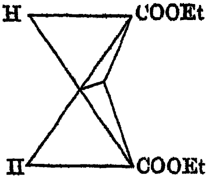
Active (racemic).



Diethylic fumarate.



Inactive.



Diethylic maleate.

From the electrolysis of diethylic dipotassium ethanetetracarboxylate as prepared by direct saponification, we might then expect the diethylic salts of both fumaric and maleic acids.

An attempt was made to separate the diethylic dihydrogen salt prepared from the dipotassium salt into its inactive constituents by fractional crystallisation. This method succeeds easily in the case of symmetrical dialkylsuccinic acids, but here we were unable to obtain any result. The compound does not crystallise well, nor does it melt sharply. Guthzeit states that it melts at 132—135° with decomposition; we did not obtain any specimens melting above 128—129°. Various metallic salts were prepared, but in no case could we separate them by crystallisation into two constituents.

The methylic salts were then substituted for the ethylic salts in the hope that they would crystallise better.

Tetramethylic Ethanetetracarboxylate.

The tetrethylic salt is usually prepared by the action of iodine dissolved in ether on diethylic sodiomalonate. We find that bromine may be used with advantage instead of iodine in the preparation of this salt and also of the tetramethylic salt.

Sodium (23 grams) is dissolved in 300 c.c. of methylic alcohol, and to the solution of sodium methoxide thus obtained dimethylic malonate (132 grams) is gradually added. The bromine (about 80 grams) may be added from a tap funnel, either as such or it may be mixed with methylic alcohol. Each drop as it falls is immediately decolorised, and the addition is continued until the solution is neutral, the point being also indicated by the persistence of the colour of the bromine. The alcohol is now distilled off on the water bath, and water added to the residue on cooling; the sodium bromide dissolves and an oily layer separates, which soon solidifies. This solid is removed and drained, first with the filter-pump and then on a porous tile. One recrystallisation from benzene affords the compound in a state of purity. The yield is 100 grams.

0·2096 gave 0·3507 CO_2 and 0·1030 H_2O. C = 45·64; H = 5·45.
$C_{10}H_{14}O_8$ requires C = 45·80; H = 5·34 per cent.

The tetramethylic salt melts at 135° and is freely soluble in the ordinary organic solvents with the exception of ether and ethylic and methylic alcohol, in which it is only moderately soluble. It is practically insoluble in water and in cold light petroleum.

Dihydrogen Dimethylic Ethanetetracarboxylate.

Tetramethylic ethanetetracarboxylate (30 grams) was dissolved in 2 litres of methylic alcohol, and to it a solution of caustic potash in methylic alcohol was added sufficient for half saponification; the mixture was then allowed to remain over night in the cold. Nothing separated, but on distilling off the alcohol, a copious white precipitate was obtained after a certain concentration had been reached. The liquid was then cooled, and the precipitate collected and drained; a potassium estimation showed that it was almost pure dipotassium dimethylic ethanetetracarboxylate. A further quantity of less pure potassium salt was obtained by evaporating the filtrate to dryness. The dipotassium salt is deliquescent, and very easily soluble in water. Its solution gives dense white precipitates with solutions of silver nitrate, lead nitrate, and mercuric chloride. With ferric chloride, it gives a reddish-brown precipitate, but with the other metallic salts practically no precipitates are obtained, unless the solutions are very concentrated. The silver salt is very sensitive to light.

The dihydrogen salt was prepared by acidifying the dipotassium salt with hydrochloric acid, and extracting the solution with ether. The behaviour of the compound obtained was very similar to that of the dihydrogen diethylic salt. It dissolved readily in organic solvents, with the exception of the aromatic hydrocarbons, and showed little tendency to crystallise well. The melting point was ill-defined. It seemed impossible, therefore, to separate the two stereomeric modifications directly by crystallisation, so the various soluble salts were studied with a view to finding one which would afford definite crystals. The salts which yielded the best results were the ammonium salt and the zinc salt. The zinc salt, being the less soluble, was prepared in some quantity by boiling the hydrogen salt with excess of freshly precipitated zinc hydroxide. After filtering, the solution was evaporated on the water bath, during which operation a small quantity of an oil was observed to separate. When the concentration had proceeded to some extent, crystals were observed to form, and the solution was then cooled and allowed to evaporate further at the ordinary temperature. Two apparently different kinds of crystals separated, one in the form of hexagonal plates, the other in needles. These were removed from the mother liquor, and an attempt made to recrystallise them. Addition of water, however, precipitated a white flocculent substance, in all probability a basic zinc salt. Repeated attempts to separate the two kinds of crystals met with no success. The ammonium salt was found to be too soluble to allow of fractional crystallisation.

The dihydrogen salt prepared from the purified zinc salt melted and decomposed at 158—160°, but did not crystallise well.

0·0795 required 6·83 c.c. decinormal soda solution for neutralisation. Replaceable hydrogen = 0·859 per cent.

Calculated for $H_2C_6H_8O_8$ = 0·855 per cent.

Electrolysis of Dipotassium Dimethylic Salt.

The dipotassium dimethylic salt was dissolved in somewhat less than its own weight of water, the solution being then extracted with ether, and filtered to remove a slight residue. The electrolysis was conducted as described by Walker and Henderson (this vol. p. 338). As the electrolysis progressed, the solution became dark coloured, and for a long time no ethereal substance was observed to separate. Finally, however, when the solution had become very concentrated by evaporation and electrolytic decomposition of the water, a small quantity of an oily substance separated along with crystals of potassium hydrogen carbonate; when no further increase in the quantity of the latter could be observed, the current was stopped, and the contents of the crucibles diluted. The oily drops partially solidified to a dark brown crystalline mass, which was freed from the small quantity of oil that adhered to it by spreading the crystals on a porous tile; it was then recrystallised thrice from alcohol. The colourless crystals thus obtained melted at 103°, and gave the following numbers on analysis.

0·1561 gave 0·2867 CO_2 and 0·0786 H_2O. C = 50·09; H = 5·59.

$C_6H_8O_4$ requires C = 50·00; H = 5·56 per cent.

The substance had thus the composition and melting point of dimethylic fumarate. It did not react with bromine in chloroform solution at the ordinary temperature, but when heated with it for 30 minutes at 100° in a sealed tube, it was converted into a dibromide. The crystalline product obtained on evaporating the chloroform and excess of bromine, separated from hot light petroleum in the form of pearly scales, which melted at 57°. Anschutz gives the melting point of the dimethylic salt of symmetrical dibromosuccinic acid as 61·5—62°.

As the corresponding methylic salts of maleic acid and isodibromosuccinic acid are liquid, there can be no doubt that the substances we obtained were fumaric acid derivatives. The ethereal product of electrolysis is obtained in so small amount that we were unable to identify the oily substance which was originally mixed with the dimethylic fumarate. It may have been dimethylic maleate or dimethylic ethinedicarboxylate; in any case, however, it formed but a very small proportion of the whole ethereal product.

We thus see that the electrolysis of dipotassium dimethylic ethanetetracarboxylate yields at least one of the products which the analogy with succinic acid would suggest.

From the spent solution, a large quantity of the dihydrogen salt was recovered on acidification and extraction with ether. The melting point remained unchanged, namely, 158—160°.

Methylic Triethylic Ethanetetracarboxylate.

On one occasion, in the preparation of the tetramethylic salt, ethylic alcohol was by an oversight used as solvent instead of methylic alcohol. The synthesis, however, was continued, in order to ascertain to what extent the ethylic group would replace the methylic group. As Purdie has shown (*Ber.*, 1887, **20**, 1555), one alkyl is very easily substituted for another in presence of sodium alkyloxide, that is, under the conditions which obtain in a malonic ether synthesis. The product of the synthesis was worked up as described under the tetramethylic salt, which it resembled closely in external appearance. On recrystallisation, however, from light petroleum, the fine, needle-shaped crystals were found to melt at 58°, the melting point of the tetrethylic salt being 76°. The following results were obtained on analysis.

0·1468 gave 0·2762 CO_2 and 0·0911 H_2O. C = 51·31; H = 6·88.

0·1632 „ 0·3072 CO_2 and 0·0982 H_2O. C = 51·33; H = 6·68.

Calculated for $C_{13}H_{20}O_8$: C = 51·31; H = 6·58 per cent.

The substance has thus the composition of the triethylic monomethylic salt. That it is not a mixture was proved by the melting point remaining at 58° after nine successive recrystallisations. The action of ethylic alcohol and sodium ethoxide under the conditions employed was therefore to replace three methyl groups by ethyl groups, the fourth methyl group remaining unattacked.

Dimethylic Diethylic Ethanetetracarboxylate.

Another instance of the replacement of one alkyl group by another was observed in an attempt to prepare the ethylic trimethylic salt from the potassic trimethylic salt and ethylic bromide. The two reacting substances were heated together at 100°, with a little ethylic alcohol, in a soda-water bottle. Potassium bromide separated, and from the solution an oil was obtained, which distilled at 200—203° under 18 mm. pressure. The substance was somewhat viscid, and did not solidify in a freezing mixture.

0·1864 gave 0·3386 CO_2 and 0·1078 H_2O. C = 49·54; H = 6·42.
0·1810 „ 0·3280 CO_2 and 0·1030 H_2O. C = 49·44; H = 6·32.
Calculated for $C_{12}H_{18}O_8$: C = 49·65; H = 6·21 per cent.

It is therefore one of the diethylic dimethylic salts, and one methyl group in the potassium trimethylic salt has been replaced by an ethyl group from the excess of ethylic bromide employed, or from the ethylic alcohol.

LXXIX.—*New Formation of Glycollic Aldehyde.*

By Henry J. Horstman Fenton, M.A.

Experiments bearing on the constitution of the acid, $C_4H_4O_6,2H_2O$ described in a former paper (Trans., 1894, **65**, 899), are still in progress, and are now nearly completed. The study of one of the transformations of this acid has given results which may be of more general interest, so that I have considered it advisable to publish a separate account of this portion of the work.

The acid is sparingly soluble in cold water, but dissolves easily in warm water. The aqueous solution is, however, very unstable, carbon dioxide being evolved slowly at ordinary temperatures, and very rapidly if the solution is heated to 50—60°; at this temperature the decomposition is complete in a few minutes, and the liquid no longer gives the characteristic reactions of the original acid, but has the properties of an aldehyde. Fehling's solution is reduced in the cold, ammoniacal silver nitrate gives a "mirror" in the cold, a rosaniline salt decolorised by sulphur dioxide has its colour immediately restored, and when heated with caustic alkalis a deep yellow coloration is produced. When warmed with excess of phenylhydrazine acetate, the solution soon becomes cloudy and, after a time, deposits a bulky precipitate consisting of yellowish-brown leaflets.

On heating the aqueous solution, some of the aldehydic substance passes off with the steam, the distillate giving a silver mirror in the cold. If allowed to evaporate in a vacuum over sulphuric acid, the solution leaves a very viscid syrup which will not crystallise even if kept several weeks; it dissolves easily in water and in alcohol, but is nearly insoluble in ether. No crystalline compound could be obtained from it by the action of excess of saturated solution of sodium hydrogen sulphite.

The aqueous solution has an acid taste and reaction with indicators, but the neutralising power is quite insignificant as compared with the reducing power, as shown by the following experiments.

3·4153 grams of the original crystallised acid was heated with water until carbon dioxide ceased to be evolved; the solution was cooled and made up to 250 c.c.

25 c.c. of this solution required 0·2 c.c. of standard soda solution, containing 0·0125 gram NaOH, per c.c. for neutralisation, phenolphthalein being used as indicator.

20 c.c. of Fehling's solution containing 0·00881 gram Cu per c.c. required (1) 20 c.c., and (2) 20·8 c.c. of the above solution for complete reduction.

Or, one molecule of the original acid, $C_4H_4O_6,2H_2O$, after decomposition, neutralised about 1/30 mol. of NaOH, but reduced nearly 2 atoms of copper from the cupric to the cuprous state.

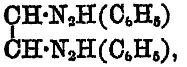
Estimation of the Carbon Dioxide evolved.—0·1516 gram of the original crystallised acid was weighed into a small distilling flask. The latter was then nearly filled with water, the neck sealed and the tube connected with a Lunge's nitrometer charged with mercury. The flask was heated in a water-bath until evolution of carbon dioxide had ceased, and the liquid was then boiled so as to tranfer all the gases to the nitrometer. The carbon dioxide was afterwards estimated by absorption with caustic potash. 37·1 c.c. of carbon dioxide was obtained at 12° and 752 mm. = 35·06 c.c. corr. If 1 mol. of the acid loses 2 mols. of carbon dioxide the volume should be 36·7 c.c.

The properties of the aldehydic substance correspond closely to those of *glycollic aldehyde*, $CH_2(OH)\cdot COH$, as described by Fischer and Landsteiner (*Ber.*, 1892, **25**, 2549), and the formation of this aldehyde in the above decomposition could be readily understood if the change takes place according to the equation

$$C_4H_4O_6 = C_2H_4O_2 + 2CO_2.$$

Glycollic aldehyde, or diose, was obtained in solution by Fischer and Landsteiner by the interaction of bromaldehyde, $CH_2Br\cdot COH$, and baryta-water at 0°. Marckwald and Ellinger also describe its formation from glycol-acetal, $CH_2(OH)\cdot CH(OC_2H_5)_2$, and dilute acids (*Ber.*, 1892, **25**, 2984). In this manner a strong solution was obtained.

The nature of the substance in solution was proved by Fischer and Landsteiner in the following way. 1st. By the action of excess of phenylhydrazine acetate, the phenyl-osazone of glyoxal



$$\begin{array}{l} CH\cdot N_2H(C_6H_5) \\ | \\ CH\cdot N_2H(C_6H_5), \end{array}$$

was obtained. 2nd. Oxidation with bromine gave glycollic acid. About 2 grams of calcium glycollate were obtained from 11 grams of the bromaldehyde. These methods of proof were adopted in the present case with the following results.

1. About 2 grams of the original acid, $C_4H_4O_6,2H_2O$, were heated with water on a water-bath until no more gas was evolved. The solution was cooled, then mixed with about 4 grams of phenylhydrazine dissolved in acetic acid, and the mixture kept at 40° in a regulated air-bath for about 24 hours. The abundant yellowish-brown crystalline precipitate produced was filtered off, drained by the aid of a pump, washed with small quantities of cold alcohol, and recrystallised from alcohol; thus obtained, the substance had the appearance of small rosettes of minute brownish-yellow plates or needles. The melting point of the specimen was 169·5°.

These properties exactly coincide with those of glyoxal phenylosazone (Pickel, *Annalen*, 1886, **232**, 231).

0·1596 gave 33·1 c.c. nitrogen at 20° and 742 mm. N = 23·66.
0·1673 gave 0·4311 CO_2 and 0·0879 H_2O. C = 70·27; H = 5·83.
$C_{14}H_{14}N_4$ requires C = 70·58; H = 5·88; N = 23·53 per cent.

2. About 15 grams of the original acid were heated with water as before, mixed, after cooling, with the calculated quantity of bromine, about 13 grams, the mixture well shaken, and allowed to stand at the ordinary temperature for two days. It was then heated on a water bath until the slight excess of bromine was expelled, cooled, neutralised with lead carbonate, filtered, and the lead removed from the filtrate by hydrogen sulphide. The excess of hydrogen sulphide was removed by heating on a water-bath, the liquid was cooled, and moist silver oxide added to remove hydrogen bromide; the silver was then removed from the filtrate by hydrogen sulphide and the excess of the latter removed as before. The solution was now well shaken with pure chalk heated on a water bath, and the filtered liquid concentrated by evaporation; the crude calcium salt which separated, when dried in the air, weighed about 6 grams.

By recrystallising from hot water, this salt was obtained in characteristic stellar groups of needles. It was dried at 120° and analysed.

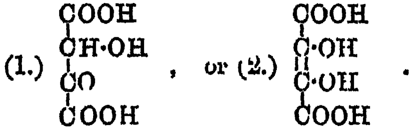
0·2385 gave 0·1700 gram $CaSO_4$. Ca = 20·96.

Calcium glycollate $(C_2H_3O_3)_2Ca$ requires Ca = 21·05 per cent.

From the above results, it may be concluded that the original acid, $C_4H_4O_6$, when heated with water, splits up almost quantitatively into glycollic aldehyde (1 mol.) and carbon dioxide (2 mols.). This reaction affords a very simple method for the preparation of glycollic aldehyde.

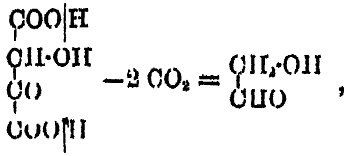
The water seems to be essential in bringing about this change, since the anhydrous acid may be heated even at 100° (in an inert atmosphere), or its solution in absolute alcohol may be boiled, at any rate for a considerable time, without any decomposition taking place; again, the anhydrous acid may be boiled with benzene without change, but on the addition of a few drops of water to the hot mixture, an immediate evolution of carbon dioxide occurs.

The nature of this change may easily be conjectured, whichever of the two possible formulæ for the original acid be adopted.



$$(1.)\ \begin{array}{l}COOH\\ \vert\\ CH{\cdot}OH\\ \vert\\ CO\\ \vert\\ COOH\end{array}\ ,\quad \text{or}\ (2.)\ \begin{array}{l}COOH\\ \vert\\ C{\cdot}OH\\ \Vert\\ C{\cdot}OH\\ \vert\\ COOH\end{array}\ .$$

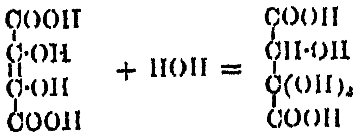
In the first case, the loss of $2CO_2$ from the carboxyl groups would leave glycollic aldehyde as a residue



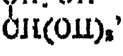
$$\begin{array}{l}COO\vert H\\ \vert\\ CH{\cdot}OH\\ \vert\\ CO\\ \vert\\ COO\vert H\end{array} - 2\,CO_2 = \begin{array}{l}CH_2{\cdot}OH\\ \vert\\ CHO\end{array}\ ,$$

this behaviour being analogous to that of acetonedicarboxylic acid, which under similar conditions loses $2CO_2$, leaving acetone.

In the second case, it may be supposed that a molecule of water is first added



$$\begin{array}{l}COOH\\ \vert\\ C{\cdot}OH\\ \Vert\\ C{\cdot}OH\\ \vert\\ COOH\end{array} + HOH = \begin{array}{l}COOH\\ \vert\\ CH{\cdot}OH\\ \vert\\ C(OH)_2\\ \vert\\ COOH\end{array}$$

and that this unstable trihydroxysuccinic acid loses $2CO_2$, as before, leaving glycollic aldehyde hydrate,  $\begin{array}{l}CH_2{\cdot}OH\\ \vert\\ CH(OH)_2\end{array}$, which then gives the aldehyde and water. The latter view is, in my opinion, by far the more probable because, as just stated, water is necessary to the decomposition, and also for other reasons which favour the second formula rather than the first. These reasons I hope shortly to communicate.

The residue obtained when the aqueous solution of the aldehyde is evaporated in a vacuum was next studied; 3·1233 grams of the original crystallised acid were decomposed, as before, by heating with water, precautions being taken to prevent loss by spurting, the solution allowed to evaporate in a vacuum desiccator over sulphuric acid, and the resulting thick syrupy residue weighed, and kept in the vacuum desiccator until the weight was constant. The residue then weighed 1·1210 grams. If the decomposition takes place quantitatively, according to the equation given above, the weight should be 1·0184 grams.

Combustion of this residue gave C = 37·33. H = 6·09 per cent.
Glycollic aldehyde requires C = 40 00. H = 6·66 per cent.

From these results, and from the slight acidity mentioned above, it is evident that a small quantity of some oxidation product is present.

If the decomposition of the original acid be effected in an atmosphere of hydrogen the quantity of this oxidation product is diminished. Thus, a sample of the residue obtained when this precaution was taken gave on analysis C = 38·53: H = 6·34.

After several trials, it has been found possible to remove this oxidation product altogether. The solution obtained after decomposition of the original acid by heating with water, is cooled and shaken for about 15 or 20 minutes with excess of pure precipitated chalk; it is then filtered, and the filtrate allowed to evaporate in a vacuum over sulphuric acid. The resulting thick syrup is digested with cold absolute alcohol, which readily dissolves the aldehyde but leaves a small quantity of a residue consisting of a calcium salt;* the alcoholic solution of the aldehyde is then allowed to evaporate, as before, in a vacuum desiccator. The residue is an almost colourless, very viscid, syrup, having a slightly sweet taste; when dissolved in water, it exhibits all the characters mentioned above. Traces of alcohol are still retained in this product, as shown by the taste, and by the somewhat high numbers obtained on analysis. After about 24 hours' exposure in a vacuum desiccator the numbers were C = 42·40; H = 7·30, but after about six days' exposure, with occasional stirring, the result was C = 40·81; H = 7·01.

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* The calcium salt, after being thoroughly washed with alcohol to remove the aldehyde, dissolves in water, and the solution gives a silver mirror on warming with ammoniacal silver nitrate. If the solution be treated with aniline oxalate and filtered from calcium oxalate, the filtrate, on standing for some time, gives a bright orange precipitate. From these observations, it may be concluded that the oxidation product above mentioned is probably *glyoxylic acid*.

In order to remove these traces of alcohol, the product was washed several times with anhydrous ether. In this case traces of ether are retained in a similar manner, even after long exposure in a vacuum desiccator; but by heating under greatly diminished pressure (about 50—20 mm.) on a water bath, the ether may be completely expelled. Thus, a specimen treated in this way gave, after about two hours' heating, the following numbers.

0·1511 gave 0·2249 CO_2 and 0·0899 H_2O. C = 40·59; H = 6·60.

The same specimen heated further for about an hour.

0·1225 gave 0·1802 CO_2 and 0·0710 H_2O. C = 40·11; H = 6·43.
Glycollic aldehyde, as above stated, requires C = 40·00; H = 6·66 per cent.

The substance, however, when heated in this way undergoes a marked change in properties. The nearly colourless syrup is transformed into a transparent, pale yellow, solid gum. This gum is now nearly insoluble in absolute alcohol; it dissolves easily, however, in water, giving a solution which has a decidedly sweet taste. The aqueous solution reduces Fehling's solution in the cold, and gives a silver mirror in the cold, just as did the original aldehyde, and it gives a deep yellow coloration when heated with caustic alkalis; but it only very slowly and imperfectly restores the colour to a rosaniline salt decolorised by sulphur dioxide, whereas the original aldehyde produced an immediate effect with this reagent. Heated to 40° with excess of phenylhydrazine acetate, a lemon-yellow, flocculent precipitate is produced, which darkens on heating to a higher temperature on a water bath. This precipitate dissolves with some difficulty in hot water, and separates, on cooling, in lemon-yellow flocks; in hot benzene or chloroform, it is more readily soluble. Examined under the microscope it is seen to consist of minute needles. The product was purified (*a*) by twice recrystallising from hot water and then from benzene, and (*b*) by recrystallising three times from benzene; both specimens melted at the same temperature, namely, 162—163°. The properties of this substance are very similar to those of the osazone which Fisher and Landsteiner obtained from tetrose, and which is identical with phenylerythrosazone. These authors showed that a solution of glycollic aldehyde mixed with weak soda solution, and kept at 0°, was changed into tetrose, the latter being identified by formation of its osazone. It seemed probable, therefore, that this same condensation might have taken place in the present case, and that the sweet, gummy substance mentioned above might be tetrose; the melting point of the osazone is, however, too low, phenylerythrosazone melting at 166—168°. In order to decide this question, the molecular weight of the gummy product was determined by Raoult's method. Water was found to be the most convenient solvent, and gave very concordant results, but with acetic acid the results were not satisfactory owing to the extreme slowness with which the substance dissolved.

The following were the results obtained.

	Grams of substance.	Grams of water.	Freezing point.		Mol. wt.
			Solvent.	Solution.	
I....	0·2622	17·72	1·847	1·692	181
II....	0·1897	15·14	3·260	3·126	177
III....	0·3447	15·14	3·260	3·025	184

These point conclusively to the formula $C_6H_{12}O_6$ (molecular weight = 180). The gummy product obtained by polymerisation of glycollic aldehyde, in the manner described above, appears therefore to be some form of *hexose*.

I hope soon to make further observations on the properties of this substance and of glycollic aldehyde.

University Chemical Laboratory,
Cambridge.

LXXX.—*Some Derivatives of Humulene.*

By Alfred C. Chapman, F.I.C.

In a former communication to the Society on the essential oil of hops (Trans., 1895, **67**, 54), I described the preparation from the oil, by fractional distillation, of a new sesquiterpene for which the name humulene was suggested. In the paper referred to, the chief physical constants of this hydrocarbon were given and a crystalline nitrosochloride melting at 164—165° was described, as also a well-crystalline nitrol-piperide (m. p., 153°), obtained by acting on the nitrosochloride with an excess of piperidene. Since the publication of this paper, I have made a further study of humulene, and have succeeded in preparing from it the following compounds.

Hydrochloride of Humulene Nitrol-piperide.

On passing dry hydrogen chloride into a solution of the nitrol-piperide in ether, a dense, white, curdy precipitate immediately falls;

this was collected and recrystallised either from boiling water or from alcohol. From the former solvent, it crystallises in hard nodular masses.

0·245 gave 0·0985 AgCl. Cl = 9·95.
$C_{15}H_{24}NO{\cdot}NC_5H_{10},HCl$ requires Cl = 10·01 per cent.

The platinochloride of this salt was prepared by mixing alcoholic solutions of platinic chloride and of the salt. It crystallises from alcohol in reddish needles which melt at 187—189°, at the same time undergoing considerable decomposition.

0·3297 gave 0·062 Pt. Pt = 18·80.
$(C_{15}H_{24}NO{\cdot}NC_5H_{10})_2,H_2PtCl_6$ requires Pt = 18·79 per cent.

Humulene Nitrolbenzylamine.

On heating humulene nitrosochloride with an excess of benzylamine almost to the boiling point of the latter, a very vigorous action occurred, the mixture becoming almost solid. On adding sufficient alcohol to dissolve the whole of the products, then a little water, and allowing the solution to stand, the nitrolbenzylamine crystallised out in considerable quantity. It was purified by recrystallisation from boiling alcohol, from which it separates in bunches of very small needles, radiating from a centre. It melts at 136°.

0·200 gave 14·0 c.c. moist nitrogen at 7° and 757 mm. N = 8·35.
$C_{15}H_{24}NO{\cdot}NH{\cdot}CH_2{\cdot}C_6H_5$ requires N = 8·24 per cent.

On dissolving this compound in dry ether and passing hydrogen chloride into the solution, a white granular precipitate of the hydrochloride formed; this is more soluble in ether than the corresponding nitrolpiperide compound. It was purified by recrystallising it several times from boiling water. It melts at 187—189°, but at this temperature undergoes some decomposition.

0·197 gave 0·0745 AgCl. Cl = 9·34.
$C_{15}H_{24}NO{\cdot}NH{\cdot}CH_2{\cdot}C_6H_5,HCl$ requires Cl = 9·42.

Humulene Nitrosate, $C_{15}H_{24}N_2O_4$.

A mixture of 5 volumes of humulene, 5 volumes of amylic nitrite, and 8 volumes of glacial acetic acid was cooled in a freezing mixture to about —15°. To this solution, a well-cooled mixture of equal volumes of nitric acid and glacial acetic acid was added little by little, with constant shaking; there was considerable evolution of heat and a white crystalline substance soon formed, the mixture becoming almost solid. Alcohol was now added, and after the contents of the tube had been allowed to remain in the cold for about an hour the substance was collected with the aid of a pump, and washed with cold alcohol. The air-dried substance was found to be practically insoluble in alcohol and ether, but fairly readily soluble in benzene, chloroform, and glacial acetic acid on warming. It crystallises best from hot benzene in the form of extremely small colourless needles, often forming rosettes on the side of the containing vessel. It melts at 162—163°, but at this temperature there is considerable blackening and escape of gas.

0·112 gave 0·085 H_2O and 0·251 CO_2. C = 61·07; H = 8·40.
0·204 „ 16·2 c.c. moist nitrogen at 6° and 750 mm. N = 9·53.
$C_{15}H_{24}N_2O_4$ requires C = 60·81; H = 8·11; N = 9·46 per cent.

When this compound was heated with piperidine, the elements of hydrogen nitrate were removed and the nitrolpiperide before described, melting at 153° was obtained as in the case of the nitrosochloride.

It is interesting in this connection to note that Wallach (*Annalen*, 1894, **279**, 392) has described an analogous compound obtained from caryophyllene. This nitrosate appears to resemble the one just described in its crystalline form and solubility, but melts at 148—149°. On boiling the nitrosate with an alcoholic solution of sodium ethoxide, no visible action occurred, but on heating the compound with the same solution in a closed vessel to the boiling point of water, it gradually disappeared, and was replaced by a dense precipitate of sodium nitrate. After filtering and evaporating the alcohol, a gummy mass remained which would not crystallise either from alcohol or ether, and which decomposed when distilled under a pressure of 20 mm.

Nitrosite of Humulene, $C_{15}H_{24}N_2O_3$.

To a mixture of equal volumes of humulene and light petroleum, a concentrated aqueous solution of sodium nitrite was added and the mixture thoroughly cooled; a volume of glacial acetic acid equal to that of the humulene taken was then added little by little with frequent shaking. The upper hydrocarbon layer rapidly acquired a deep blue colour, which, on standing for some time, became somewhat green. From this green layer, deep blue needles soon separated, which, after some hours, were collected and purified by one recrystallisation from boiling alcohol, from which solvent it separated in the form of magnificent, blue needles.

Two separate preparations gave the following results on analysis.

0·2085 gave 18·5 c.c. moist nitrogen at 18° and 762 mm. N = 10·24.
0·207 „ 17·8 „ „ at 15° and 756 mm. N = 10·04.
$C_{15}H_{24}N_2O_3$ requires N = 10·00 per cent.

The oily mother liquors from which the above crystals were obtained deposited a further quantity of needles of a paler colour than the above, and the mother liquors from these in turn deposited needles, which, after crystallisation from alcohol, were colourless. This compound, which could only be obtained in small quantity, gave the following numbers on analysis.

0·203 gave 17·5 c.c. moist nitrogen at 18° and 758 mm. N = 9·93.
$C_{15}H_{24}N_2O_3$ requires N = 10·00 per cent.

From this it appears that the white compound is isomeric with the blue, the latter being the nitroso- the former the isonitroso-derivative of humulene. This conclusion is borne out by determinations of the melting points of the two compounds given below, and by the almost complete conversion of the blue into the white by the long-continued boiling of its alcoholic solution.

Several preparations of the blue compound, purified by one crystallisation from alcohol, melted at about 120°, the effect of each subsequent recrystallisation from the same solvent being to very considerably increase its melting point and to render the substance paler in colour. The melting point of several preparations of the white compound obtained both from the original mother liquors and also by the boiling of an alcoholic solution of the blue compound, was 166—168°, at which temperature it underwent some decomposition, melting to a brownish liquid. The blue crystals also undergo some decomposition when heated to their melting point, forming a greenish liquid.

As an example of the effect of boiling alcohol on the blue compound, I may give the following numbers.

A preparation of the blue needles, after one recrystallisation from alcohol, melted at 120—121°. A second recrystallisation from the same solvent raised the melting point to 140°, the crystals obtained being much paler in colour. They were then dissolved in alcohol and boiled for several hours; the needles which separated on cooling had only a very faint blue tinge and melted at 165—168°. Two other experiments gave similar results, although the final melting point was not quite so high.

The blue nitrosite dissolves readily in hot alcohol, glacial acetic acid, ether, and chloroform, giving in all cases blue solutions, but is practically insoluble in light petroleum. Of the few blue solid nitroso-compounds at present known, the nitrosochloride of tetramethylethylene described by Thiele (*Ber.*, 1894, **27**, 455) is, perhaps, the most interesting, since, as Tilden has pointed out (Trans., 1894, **65**, 324), it must be a true nitroso- and not an iso-nitroso-compound, as there is no hydrogen directly united to the two ethylenic carbon atoms. It is, of course, well known that many other compounds containing the NO group, though colourless when crystallised, are blue when melted or when in solution, such as the pseudonitrols, nitrosobenzene, &c., and Tilden (Trans., *loc. cit.*) has suggested that the blue or green colour, which is so frequently observed when nitrosyl chloride and nitrous anhydride unite with unsaturated hydrocarbons, is to be regarded as an indication of the formation of a true nitroso-compound as the first step in the process, the colourless compound which afterwards separates out being probably an oxime. The experiments above described afford strong proof of the correctness of this suggestion.

LXXXI.—*A Colouring Matter from* Lomatia ilicifolia *and* Lomatia longifolia.

By Edward H. Rennie, M.A., D.Sc., Professor of Chemistry in the University of Adelaide, South Australia.

INTRODUCTORY AND THEORETICAL PART.

Some time ago, by the kindness of Mr. J. H. Maiden, Director of the Technological Museum, Sydney, the author was supplied with a quantity of the seeds of *Lomatia ilicifolia* and *Lomatia longifolia*, two species of the genus Lomatia (order Proteaceæ) growing on the elevated portions of south-eastern New South Wales and north-eastern Victoria. These seeds are more or less surrounded by the yellow substance which forms the subject of this investigation. A preliminary examination soon showed that the colouring matter is the same for both species, and that it is closely allied to the "lapachol" described by Dr. Hooker (Trans., 1892, 61, 611).

On boiling with water slightly acidified with acetic acid, the yellow substance is easily extracted, and may be purified by crystallisation from hot water (slightly acidified with acetic acid). It forms yellow needles, melting at 127°, soluble in hot water, and separating in the crystalline form on cooling, easily soluble in alcohol, ether, and the ordinary solvents. It dissolves easily in alkalis, forming a deep red solution, from which it is precipitated unchanged on the addition of an acid. Its formula, as ascertained by several combustions and by a molecular weight determination, as also by collateral evidence (detailed below), is $C_{15}H_{14}O_4$. It contains two hydroxyl groups, as evidenced by the formation of a diacetyl derivative on treatment with acetic anhydride. It forms also metallic derivatives, of which the barium compound is the most important yet examined, exhibiting, as it does, remarkable similarity to the barium salt of hydroxyhydrolapachol described by Hooker (*loc. cit.*).

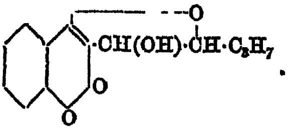
So great is this similarity, and so close is the percentage of barium found to that required for the barium salt of hydroxyhydrolapachol, that at first there seemed to be a probability of the identity of the substance under examination with hydroxyhydrolapachol. As, however, the results of ultimate analysis pointed to a distinct difference, the author applied to Dr. Hooker, who very kindly forwarded small specimens of hydroxyhydrolapachol and of some other lapachol derivatives for comparison. On comparing the substances, it was soon seen that they are not identical. Hydroxyhydrolapachol seems to be but very sparingly soluble even in boiling water (nothing is said on this point in Dr. Hooker's paper), whereas, as stated above, the lomatia colouring matter dissolves to a considerable extent and crystallises on cooling. Further, the specimen of hydroxyhydrolapachol forwarded by Dr. Hooker melted sharply at 125°, the same thermometer being used as was employed in determining the other melting points in this paper. In fact, when specimens of the two substances were tried simultaneously with the same thermometer, the one melted at 125° and the other at 127°.

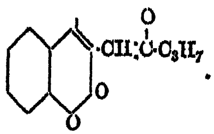
On oxidation with chromic mixture the new substance yields acetic acid, and sometimes, if the oxidation be gently managed, phthalic acid.

If the substance is dissolved in a small quantity of concentrated sulphuric acid, and if the solution, *after standing for about* 20 *minutes*, be poured into a quantity of cold water, a small quantity of tarry matter separates; on filtering this off and allowing the clear solution to remain for several days, beautiful rosettes of *red* crystals gradually form on the bottom and sides of the beaker, and can be easily purified by crystallisation from somewhat diluted alcohol. This new substance melts at 204—205°, and is isomeric with the original yellow substance. If it be boiled for a few minutes with a strong solution of caustic potash, it dissolves forming a deep red solution, and this solution on acidification deposits a yellow crystalline substance, which, after purification, melts at 182°. The two last-mentioned compounds would seem, judging from the results of analysis, and from the melting points, to be identical with Hooker's hydroxy-β-lapachone and dihydroxyhydrolapachol respectively. It is true that the melting point of the red substance is about 3° higher than that given by Hooker (201·5°) for hydroxy-β-lapachone, but that might easily arise from some slight difference in purity. The melting point of the yellow substance is, however, identical with that given by Hooker for dihydroxyhydrolapachol. If this supposition be correct (it is to be regretted that the quantity of material at the author's disposal was too small for an exhaustive examination), it would seem to follow that the lomatia colouring matter is *hydroxylapachol*. Just as lapachol on treatment with concentrated sulphuric acid yields β-lapachone, so hydroxylapachol should yield hydroxy-β-lapachone, and the latter on treatment with caustic potash and subsequent acidification should yield, as Hooker has shown, dihydroxyhydrolapachol.

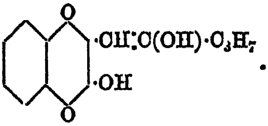
The presence of the hydroxyl group in hydroxylapachol, however, renders possible another reaction under the action of concentrated sulphuric acid, to which there appears to be no parallel in the case of lapachol. If the solution of hydroxylapachol in concentrated sulphuric acid, instead of being allowed to stand for 20 minutes, be *immediately* poured into cold water, a red crystalline substance is precipitated, which after recrystallisation from somewhat diluted alcohol melts at 110—111°; this contains the elements of a molecule of water less than hydroxylapachol, the combustion numbers indicating the formula $C_{15}H_{12}O_3$. This substance must be either identical or isomeric with Paternò's *isolapachone* if Hooker's revised formula for that substance be accepted as correct. That it is not identical is obvious from the melting point (isolapachone, according to Paternò, melts at 140—141°: Hooker does not mention its melting point), and also from the following reaction. If the substance melting at 110—111° is boiled for a few minutes with strong caustic potash it dissolves, forming a deep red liquid from which acids precipitate a yellow crystalline substance, *apparently isomeric with hydroxylapachol*, and melting at 109—110°. Now Hooker has shown (*loc. cit.*) that isolapachone separates unchanged on acidifying its solution in alkalis, the acid substance first formed being apparently converted into its internal anhydride on liberation from its salts.

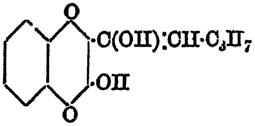
The formation of the red substance melting at 110—111° appears to constitute, as might be expected from what is stated above, an intermediate stage in the formation of hydroxy-β-lapachone, for the mother liquor after filtering off the former deposits, after many days' standing, a small quantity of red crystals melting at 204—205°, and easily recognised as identical with hydroxy-β-lapachone. This being so, it seems to the writer that if Hooker's formula for hydroxy-β-lapachone (I)

I. 

II. 

be correct, then the most probable formula for the red substance melting at 110—111° will be II, but this is the formula suggested by Hooker for Paternò's isolapachone, though he says (*loc. cit.*) "the formula must be accepted with some caution until it is based on further experimental evidence." Obviously there is need for further investigation as to the relationship of these two substances. It may be pointed out, however, that a substance of the above formula might be expected (according to Hooker's experiments in similar cases) to yield a substance of the formula III,

III. 

IV. 

This would be isomeric with the original hydroxylapachol, which as it can be converted into Hooker's hydroxy-β-lapachol by treatment with sulphuric acid should have the formula IV. The writer puts forward these views with some diffidence as he has had but a small quantity of material to work on, and no more is available at present. Should any more substance be obtained later on, the writer proposes to hand it over to Dr. Hooker, who, he understands, is still investigating lapachol and its derivatives.

EXPERIMENTAL PART.

Extraction and Purification of Hydroxylapachol.—The seeds to which the yellow substance adheres are exhausted with boiling water, slightly acidified with acetic acid, and the liquid rapidly filtered while hot; on cooling, it deposits the hydroxylapachol in a crystalline form. Two or three recrystallisations from slightly acidified boiling water usually suffice for complete purification. The substance is then seen to be perfectly homogeneous when examined by the microscope, and to consist of slender, yellow needles; the melting point after several crystallisations from varying solvents remains constant at 127°, and when submitted to combustion it gave the following results.

I.	0·2520	gram of	substance	gave	0·6455 CO_2	and	0·1300 H_2O.
II.	0·2144	,,	,,	,,	0·5500 CO_2	,,	0·1115 H_2O.
III.	0·2133	,,	,,	,,	0·5445 CO_2	,,	0·1070 H_2O.
IV.	0·2143	,,	,,	,,	0·5500 CO_2	,,	0·1045 H_2O.
V.	0·2137	,,	,,	,,	0·5449 CO_2	,,	—
VI.	0·2204	,,	,,	,,	0·5634 CO_2	,,	0·1110 H_2O.

	Found.						Calculated for
	I	II.	III.	IV.	V.	VI.	$C_{15}H_{14}O_4$.
C	69·85	69·96	69·62	69·99	69·54	69·71	69·76
H	5·73	5·77	5·57	5·42	lost	5·59	5·12

A molecular weight determination was made by the freezing point method, using glacial acetic acid as the solvent, with the following result.

Weight of substance taken......... = 0·382 gram.
Weight of solvent .... = 22·872 grams.
Depression of freezing point........ = 0·244°.

Using the constant 3860 given by Ostwald for acetic acid, this gives

$$\text{Molecular weight} = \frac{3860 \times 0{\cdot}382}{22{\cdot}872 \times 0{\cdot}244} = 264.$$

The calculated molecular weight for $C_{15}H_{14}O_4$ is 258.

Metallic Derivatives.—Hydroxylapachol dissolves easily in solutions of the caustic and carbonated alkalis, but the compounds formed are very soluble, and so far have not been obtained in a pure state.

The barium derivative, as already indicated, exhibits a great resemblance to the barium derivative of hydroxyhydrolapachol described by Hooker (*loc. cit.*), yet it presents some slight differences from that compound. It is readily prepared by boiling hydroxylapachol with water and barium carbonate. A deep crimson solution is formed, which, on cooling, usually deposits orange needles of the barium derivative. Sometimes, however, the liquid instead of depositing crystals sets to a deep claret-coloured jolly. The conditions necessary to produce this result have not, however, from want of material been determined; the usual result is the formation of the crystals referred to. These crystals when dried over sulphuric acid appear at first to be practically anhydrous, as they lose only a trifle in weight even when heated to 110—120°. Above this temperature they are apt to decompose. The following figures obtained on analysis show, however, that just as in the case of the corresponding hydroxyhydrolapachol compound these crystals are not really anhydrous, but contain one molecule of water.

I. 0·2970 gram of substance gave 0·1012 gram $BaSO_4$.
II. 0·1719 „ „ „ 0·0585 „ $BaSO_4$.
III. 0·2148 „ „ „ 0·0740 „ $BaSO_4$.
IV. 0 2078 „ „ „ 0·0723 „ $BaSO_4$.
V. 0·2075 „ „ „ 0·0718 „ $BaSO_4$.

	Found.					Calculated for
	I.	II.	III.	IV.	V.	$(C_{15}H_{13}O_4)_2Ba + H_2O$.
Ba....	20·04	20·01	20·25	20·46	20·34	20·47

In Experiments I, II, and III the substance was dried at 100°, in Experiments IV and V it was dried at 110—120°. If now the orange crystals be vigorously rubbed up in an agate mortar, they undergo a change similar to that described by Hooker in the case of the hydroxyhydrolapachol compound; this rubbing up is tedious and difficult, but the compound gradually assumes a very deep maroon colour. In this condition it is apparently amorphous, but it does not swell up and become converted into the orange crystals on mere contact with water like the corresponding hydroxyhydrolapachol compound. On boiling with water it dissolves, and on cooling the solution deposits the orange crystals. Several experiments with small quantities of material indicated that in the rubbing up process water is absorbed from the atmosphere, and that the triturated material on being heated loses more water than can be accounted for by this absorption, that in fact, it becomes converted into the anhydrous barium compound. The heating, however, needs to be carefully managed, and the temperature must not rise much above 100°, or decomposition is liable to set in. Moreover, if heat (even a temperature of 100°) be applied too suddenly the substance is partly converted into the original orange crystalline condition, and the escape of water is in some measure interrupted. Whereas if the heating be gradual the substance will retain its deep maroon colour until water ceases to come off. The following are some of the results obtained in these experiments, all of them being carried out with the triturated material, and the heating to 100° being in most cases gradual, though in some instances the material was placed at once in a water oven round which the water was boiling.

I. 0·1888 lost (at 100°) 0·0100 H_2O and yielded 0·0635 $BaSO_4$.
II. 0·2970 „ 0·0170 H_2O „ 0·0980 $BaSO_4$.
III. 0·5855 „ 0·0315 H_2O.
IV. 0·3412 „ 0·1138 $BaSO_4$.
V. 0·2773 „ 0·0128 H_2O „ 0·0925 $BaSO_4$.
VI. 1·1660 „ 0·0585 H_2O.
VII. 0·2134 „ 0·071 $BaSO_4$.

	I	II.	III.	IV.	V.	VI.	VII.
Percentage of water lost at 100°	5·29	5·72	5·39	—	4·62	5·02	–
Percentage of Ba on undried material. .	19·77	19·40	- -	19·61	19·61	—	19·56
Percentage of Ba on material dried at 100°	20·88	20·58	—	20·80	20·56	—	20·68

The absorption of water during the process of trituration is, so far as these experiments are concerned, deduced from the diminished percentage of barium; the percentage in the orange crystals being about 20·4, and in that in the triturated material 19·59 (average).

It was thought desirable, however, to confirm this by direct experiment. A weighed quantity of the orange crystals was therefore taken and very carefully rubbed up in an agate mortar on a sheet of white paper in such a way that no particles were lost. The material was then very carefully scraped out of the mortar and weighed. The mortar, pestle, and spatula used for scraping were then treated with pure hot water till all adhering substance (very small in amount) was dissolved, and the solution was evaporated in a platinum dish and converted into barium sulphate. From the weight of $BaSO_4$ thus found, the equivalent weight of the barium derivative was calculated, and this was added to the weight of the main quantity. In an actual experiment conducted in this way, 1·146 grams of the orange crystals gave 1·166 grams of triturated substance actually weighed *plus* 0·0125 gram, calculated from $BaSO_4$ as just indicated, or a total of 1·1785 grams. This is a gain of 0·0325 gram or 2·83 per cent. This is the material used in Experiment VI above, in which the total loss on heating to 100° was 5·02 per cent. It may be added that while these experiments were being conducted, the atmosphere was almost constantly humid. The figures agree fairly closely and seem to be consistent with the supposition that during trituration the orange crystals of the barium derivative absorb $1H_2O$, but that on heating the triturated material to 100°, it loses not only the water taken up, but another molecule in addition, becoming, in fact, anhydrous, or nearly so. The following figures bear out these statements when compared with the experimental results. The addition of $1H_2O$ to $(C_{18}H_{13}O_4)_2Ba + H_2O$ requires an increase in weight of 2·69 per cent., and the percentage of barium in the substance so formed would be 19·94. If, then, this substance loses $2H_2O$, the decrease in weight would be 5·24 per cent., and the percentage of barium in the anhydrous derivative would be 21·04. That the percentages of barium found in the dried material fall, in some cases, considerably short of the latter figure, is doubtless due to the fact above stated, that sometimes even with careful heating, the dark maroon-coloured compound is partly converted into the original orange crystalline condition, the escape of water being thereby prevented and the percentage of barium consequently lowered.

The calcium derivative prepared by a method similar to that used for the barium compound forms an almost black, granular mass, which under the microscope is seen to consist of very dark red crystalline grains. After having been left in a desiccator over sulphuric acid for several days, it loses water slowly at 100°, more rapidly at 120°. In one experiment 0·2712 gram prepared in this way yielded 0·0645 $CaSO_4$, which represents 6·99 per cent. of calcium;

the theoretical amount for $(C_{15}H_{13}O_4)_2Ca + H_2O$ being 6·99 per cent. One rough experiment seemed to indicate that this salt also, when rubbed up in a mortar, behaves in somewhat the same manner as the barium compound, but the data are, from want of material, insufficient to establish the point.

The silver derivative can be prepared by precipitating a solution of silver nitrate with a solution of the barium derivative. It forms a maroon-coloured, crystalline powder. On analysis 0·2304 gram gave 0·065 metallic silver = 28·21 per cent.; the theoretical number for $C_{15}H_{13}O_4Ag + H_2O$ being 28·19 per cent.

Acetyl Derivative.—To prepare the acetyl derivative, hydroxylapachol is boiled with acetic anhydride and a minute quantity of zinc chloride for two or three minutes; water is then added, the contents of the vessel heated to decompose the excess of acetic anhydride, and the whole is allowed to stand. In this way, a yellow solid is obtained, which on recrystallisation forms yellow needles, appearing quite homogeneous when examined by the microscope. After being several times recrystallised from alcohol and allowed to dry in the air, its melting point remains constant at 82°.

0·2265 gave 0·5503 CO_2 and 0·118 H_2O. C = 66·26; H = 5·79.
$C_{15}H_{12}O_4(C_2H_3O)_2$ requires C = 66·66; H = 5·26 per cent.

Two saponification experiments were performed as follows.

1. A small portion of the substance = 0·3542 gram was boiled with *pure* caustic soda till complete solution was effected, the liquid acidified with sulphuric acid, and distilled with the usual precautions, the distillate being collected in a flask containing pure barium carbonate. The distillate was then boiled with the barium carbonate, filtered, and the barium in the filtrate estimated. The $BaSO_4$ obtained weighed 0·2189 gram, and this corresponds to 0·1127 acetic acid or 31·8 per cent. The theoretical quantity obtainable from a diacetyl derivative is 35·08 per cent. and from a monacetyl derivative 20 per cent.

2. A weighed quantity of material = 0·2175 gram was boiled for some time with water and a slight excess of barium carbonate in a flask attached to a reflux condenser. As soon as saponification was complete, the excess of barium carbonate was filtered off and the barium estimated in the filtrate. The quantity of $BaSO_4$ found was 0·2094 gram, but of this only two-thirds is due to the presence of the acetyl groups, the remainder being due to the formation of the soluble barium derivative of hydroxylapachol. This is evident from the following equation.

$$2C_{15}H_{12}O_4(C_2H_3O)_2 + 3BaCO_3 + H_2O = (C_{15}H_{13}O_4)_2Ba \\ + 2(C_2H_3O_2)_2Ba + 3CO_2.$$

Two-thirds of 0·2094 = 0·1396 $BaSO_4$, which corresponds to

0·0719 gram acetic acid or 33·06 per cent. Theory, 35·08 per cent. There can be no doubt, therefore, that a diacetyl derivative is formed.

Oxidation.—On boiling with a 5 per cent. solution of potassium dichromate in dilute sulphuric acid for some hours, hydroxylapachol is almost completely oxidised, only a small quantity of tarry matter being formed. Acetic and phthalic acids were easily recognised as the products of oxidation.

Action of Sulphuric acid on Hydroxylapachol and Formation of Hydroxy-β-lapachol.—Hydroxylapachol is dissolved in a small quantity of concentrated sulphuric acid in the cold, the solution is allowed to stand for from 15 to 20 minutes, and is then thrown into a large quantity of cold water. A small quantity of tarry matter separates which can be filtered off after the liquid has been allowed to stand for a short time; a clear solution is thus obtained from which beautiful rosettes of red crystals begin to separate after an interval of from 7 to 10 days. These crystals are readily purified by two or three crystallisations from slightly diluted alcohol, and they melt at 204—205°.

0·1192 gave 0·3065 CO_2 and 0·0615 H_2O. C = 70·13*; H = 5·73.
$C_{15}H_{14}O_4$ requires C = 69·76; H = 5·42 per cent.

The melting point of this substance is slightly higher than that given by Hooker (201·5°) for hydroxy-β-lapachone. Two or three different small specimens, however, always melted at the same temperature. From the combustion numbers and the reaction with caustic potash, to be immediately described, the writer believes this substance to be identical wtth hydroxy-β-lapachone. When boiled for a few minutes with a strong solution of caustic potash, the red crystals dissolve, forming a deep red solution from which on acidification a yellow substance is precipitated; after being recrystallised two or three times from alcohol it melts at 182°. Hooker gives 181—182° as the melting point of dihydroxyhydrolapachol. The following are the results obtained by combustion.

I. 0·2486 gave 0·5938 CO_2 and 0·1320 H_2O. C = 65·14; H = 5·89.
II. 0·2280 „ 0·5445 „ 0·1198 „ C = 65·13; H = 5·83.
$C_{15}H_{16}O_5$ requires C = 65·21; H = 5·79 per cent.

From want of material, this substance could not be further studied; it was observed, however, that on boiling with concentrated hydrochloric acid it was dissolved, and a red substance was formed, which melted at 202°, and was doubtless hydroxy-β-lapachone.

Action of Sulphuric acid on Hydroxylapachol and Formation of a Red Substance differing from Hydroxy-β-lapachone.—Hydroxylapachol is dissolved in the smallest possible quantity of concentrated sulphuric acid and the solution *immediately* poured into cold water; the red crystalline substance which is precipitated is readily purified by one or two recrystallisations from slightly diluted alcohol. As thus obtained, it forms beautiful, silky needles of a somewhat deeper red than hydroxy-β-lapachone; it melts at 110—111°, is practically insoluble in water, but soluble in alcohol and the ordinary solvents.

0·1544 gave 0·4275 CO_2 and 0·0748 H_2O. C = 75·52[*]; H = 5·38.
0·1469 ,, 0·4035 ,, 0·0685 ,, C = 74·91; H = 5·11.
$C_{15}H_{12}O_3$ requires C = 75·00; H = 5·00 per cent.

After filtering off this substance and allowing the mother liquor to stand for a long time, they deposited a small quantity of red crystals melting at 204°, doubtless hydroxy-β-lapachone. Hence the above-described substance would appear to be an intermediate stage in the formation of hydroxy-β-lapachone. If the compound melting at 110—111° be boiled for a few minutes with a strong solution of caustic potash, it dissolves, and the solution on acidification deposits a yellow substance which must be recrystallised four or five times from water slightly acidified with acetic acid; it then forms yellow needles melting at 109—110°. It yielded the following results on combustion.

0·128 gave 0·3287 CO_2 and 0·064 H_2O. C = 70·04[*]; H = 5·55.
$C_{15}H_{14}O_4$ requires C = 69·76; H = 5·42 per cent.

This substance is obviously formed by the addition of the elements of water to the red compound melting at 110—111°, and is therefore isomeric with hydroxylapachol, but as in the case of some of the other substances described, there was not sufficient material for further examination; its relations to hydroxylapachol and to Paternò's isolapachone have been already discussed in the introductory part.

The author is deeply indebted to Mr. J. H. Maiden, of the Technological Museum, Sydney, for supplies of material which are difficult to obtain, and also to Dr. Hooker for specimens of some of his lapachol derivatives.

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[*] In this combustion and the subsequent ones marked with an asterisk in this paper, the somewhat high percentage of carbon is believed to be due to an imperfection in the combustion apparatus subsequently discovered.—E. H. R.

LXXXII.—*Dissociation of Liquid Nitrogen Peroxide.* Part II. *The Influence of the Solvent.*

By JAMES TUDOR CUNDALL, Lecturer on Chemistry in the Edinburgh Academy.

IN a former communication to the Chemical Society (Trans., 1891, **59**, 1076), I described some colorimetric experiments to show that liquid nitrogen peroxide dissociates, both on dilution with an "indifferent" solvent and on rise of temperature.

At the outset it was supposed that dilution would produce the same effect that is understood to result from the dilution of a dissociable gas with an indifferent gas, that is, act as a mere reduction of pressure.

This may be the case with solutions in which the nitrogen peroxide is present in concentrations comparable with gaseous peroxide, but it does not seem to be so with the solutions described in the present communication, which are of about 3 grams of peroxide to 100 c.c. of solution; roughly corresponding to the gas under a pressure of over 7 atmospheres if N_2O_4 were still obeying Boyle's law.

Ostwald has shown (Trans., 1892, **61**, 242), from the results of my experiments, that the dissociation of the liquid on dilution obeys the same law that it follows when the pressure on the gas is reduced, but that the dissociation in the liquid is nothing like so far advanced. This discrepancy was to be expected as the concentrations are so very different in the two cases, even if the solvent had no specific action. I had indeed made some calculations of a similar character previous to publication, but, owing to the great difference between the concentrations, I refrained from stating them until some more dilute solutions had been examined.*

The dissociation in the chloroform solution differing from that in the gas, it was necessary to extend the experiments to decide whether the deviation was due to the solvent or to the proportionally very great concentration of the peroxide. The first question is perhaps the most interesting, for, as Ostwald suggests, it may be similar to the influence of the solvent on the rate of chemical action. N. Menschutkin has made experiments of this kind, that is on the velocity of etherification (*Zeit. physikal. Chem.*, 1888, **1**, 611) and of interaction of ethylic iodide and triethylamine (*Zeit. physikal. Chem.*, 1890, **6**, 41), in which he clearly shows that the so-called indifferent solvent has a marked effect on the rate of change.

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* Some confusion has arisen owing to the strength of the solutions in my previous paper being stated in *volumes* of peroxide per 100 volumes of solution; the concentration or *weight* of peroxide being the percentage by volume in volume × 1·49. As, however, the absolute amount of NO_2 formed is calculated by multiplying the weight of NO_2 per 100 grams of peroxide in one of the solutions by the relative dissociation (Trans., 1891, **59**, 1089), the difference is of no consequence in the present or previous communication, but the concentration and constant in Ostwald's paper are 1/1·49 of their proper values. To avoid further misconception, I state the strengths hereafter both in volumes and weights of peroxide per 100 c.c. of solution.

The following experiments are a further contribution to our knowledge of similar actions.

Apparatus.—This was substantially the same as that employed in the former part of the work, only minor improvements having been made.

Materials used and Method of Comparison.—A fresh quantity of nitrogen peroxide (350 grams) was prepared by the method previously described (1077, *loc. cit.*), except that finely powdered commercial arsenic trioxide was used. In this case, it was found advisable to fit the generating flask with a glass dead-weight safety valve as the action was apt to be dangerously rapid at the commencement.

The active nature of nitrogen peroxide prohibits the use of a great number of liquids as solvents, although it was found that when precautions were taken to ensure dryness and purity, a larger number of them could be employed than was expected. Those which yielded good results were methylene chloride, chloroform, carbon tetrachloride, ethylene chloride, ethylidene chloride, chlorobenzene, silicon tetrachloride, bromoform, ethylic bromide, ethylene bromide, bromobenzene, carbon bisulphide and benzene. Acetic acid was not very satisfactory as it was difficult to obtain fairly large quantities absolutely dry, and even then, on standing or heating with the peroxide, some action took place.

Parachlorotoluene was either acted on slightly, or contained some impurity I could not remove. It seemed almost impossible to obtain benzylic chloride in a satisfactory state of purity and the other substances, which were carefully tried, namely, ethylic iodide and stannic chloride, were immediately acted on.

Some solutions kept better than others · the standard chloroform solutions were proved to be unaltered after six months' use, though after longer periods, especially if much heated, some slight change was detected. Carbon and silicon tetrachloride solutions keep as well, but the others, though never tested after any length of ti probably do not suffer much change. Nitrogen peroxide is a d test for water, and some other impurities in the solvents; the least trace of water, for example, causing a peculiar and easily recognised dinginess of the solution, whilst larger quantities turn dilute solutions distinctly greenish. The solutions were made up as before by weighing (a preliminary measurement of the volumes being made in order to get approximately equal strengths), and the percentage by volume in volume calculated from the relative densities at 0° unless otherwise specified. Details of the weighings and calculations of strength are omitted in order to save space.

The comparisons, made in the manner formerly described (*loc. cit.*, 1082), were with chloroform solutions, which were standardised against the pure peroxide. The individual matches, of which at least five were made for each comparison, are not stated, but only their sums, reduced to the length that matches a column of pure peroxide 10 mm. long. I found that with practice I could make the individual matches of a comparison more concordantly than those cited formerly.

Influence of External Pressure.—The colorimeters used (fig. 1, 1079, *loc. cit.*) being sealed, it was necessary to settle whether alterations of pressure on the liquid would affect the colour, as such alterations are liable to take place from the expansion of the liquid or variation of its vapour pressure.

To settle the question, the side tube of a colorimeter, containing a solution 1 Y, was opened to the atmospheric pressure of 770 mm., and its contents matched against a standard solution 3 C′, both being kept at temperature of 15·7°. It was found as a mean of 5 readings that 106·6 mm. of 1 Y matched 100 of 3 C′. The open colorimeter was then connected with a supply of compressed air at an additional pressure of 640—700 mm., and readings again taken. It was then found as a mean of 8 readings that 105·8 mm. of 1 Y matched 100 of 3 C′. The difference between the two results is within the experimental error. This is as may be expected, for, as the solutions are practically incompressible, any influence from the molecules being brought closer together by such pressures is out of the question. The pressure on the liquids is therefore neglected.

Solutions in Chloroform.

Chloroform, purified as previously described (*loc. cit.*, 1078), was made up into a solution 1 C of 1·84 c.c., or 2·74 grams of nitrogen peroxide in 100 c.c. of solution. The solution was compared with pure nitrogen peroxide on four different occasions, and though the comparison is a difficult one, owing to the very different strengths of the solutions, the results are very concordant.

TABLE I.—*Comparison at different temperatures of Solution* 1 *C of a strength of* 1·84 *c.c. or* 2·74 *grams per* 100 *c.c. of Solution, with pure Nitrogen Peroxide at* 0°. *A column* 10 *mm. long of the pure peroxide is taken as the unit of colour and as being dissociated to the extent of* 1 *unit* (1 *unit of dissociation* = 0·0468 *part by weight of* NO_2 *in* 100 *parts by weight of peroxide*).

Date.	Columns of equal tint.	Temperature.	Solution.	Per cent. × length.	Relative dissociation.
25/5/93	10 mm.	0° C	Peroxide	1000	1·0
,,	164 ,,	0	1 C	302	3·3
,,	53 ,,	12·8	1 C	98	10·2
26/5/93	165 ,,	0	1 C	304	3·3
,,	66 ,,	12·7	1 C	121	8·3
12/7/93	168 ,,	0	1 C	306	3·3
,,	80 ,,	7·5	1 C	147	6·8
,,	49 ,,	14·7	1 C	90	11·1
4/12/93	162 ,,	0	1 C	299	3·4
,,	101 ,,	6·1	1 C	186	5·4

The comparison of solution 1 C at higher temperatures with the pure peroxide was not made directly, but by means of two solutions in carbon tetrachloride. The chloroform solution was compared with the carbon tetrachloride solution at about 12°, and the relation

TABLE II.—*Indirect comparison of Solution* 1 *C with the pure Peroxide at* 0° *through Solution* 1 *T. From results in Table I,* 60 *mm. of* 1 *C at* 11·8° *are taken as being equal to* 10 *mm. of pure peroxide.*

Columns of equal tint.	Temperature.	Solution.	Per cent. × length.	Relative dissociation.
10 mm.	0°	Peroxide.	1000	1·0
(60) ,, (basis) .	(11·8)	(1 C)	(111)	(9·0)
51 ,, ...	11·8	1 T	—	—
46 ,, ...	19·1	1 C	85	11·8
24 ,, ...	28·0	1 C	44	23·0
13 ,, ...	36·0	1 C	24	42·0
9 ,, ...	42·0	1 C	17	59·0
Through Solution 2 *T.*				
86 mm.	12·1°	2 T	—	—
36 ,, ...	19·8	1 C	66	15·0
22 ,, ...	29·0	1 C	41	24·0
11 ,, ...	39·7	1 C	21	48·0

between the colours found, and hence from the results in Table I, the relation between the colours of the carbon tetrachloride solutions and the pure peroxide.

The carbon tetrachloride solutions were then kept at the same temperature, and compared with the chloroform solution at varying temperatures. The colour of the carbon tetrachloride solution in terms of that of a column of the pure peroxide being known, proportion gives the relative colour of solution 1 C compared with that of a 10 mm. column of pure peroxide at 0°.

A solution in chloroform, 2 C, of 1·79 volumes of peroxide in 100 volumes of solution was made up as a check on solution 1 C, and compared, with the following results

Cols 1 C.	Cols. 2 C.	Temp
100	106	9·3°
100	110	12·8

As there was no important difference in tint, on allowance being made for the difference in strength, solution 2 C was not preserved as a standard.

Owing to an accident, the colorimeter containing 1 C ceased to work well, so a solution of 3 C of 1·90 volumes of peroxide per 100 volumes of solution was made up and put into a new colorimeter.

Solution 3 C was then compared with 1 C, when it was found that 100 mm. 1 C matched 100 mm. 3 C at 10·5°. A portion of solution 3 C was then used as the standard of comparison instead of solution 1 C, a second portion being stored in a sealed bulb in a cool dark place, and used in the most recent experiments as a standard under the title of 3 C′.

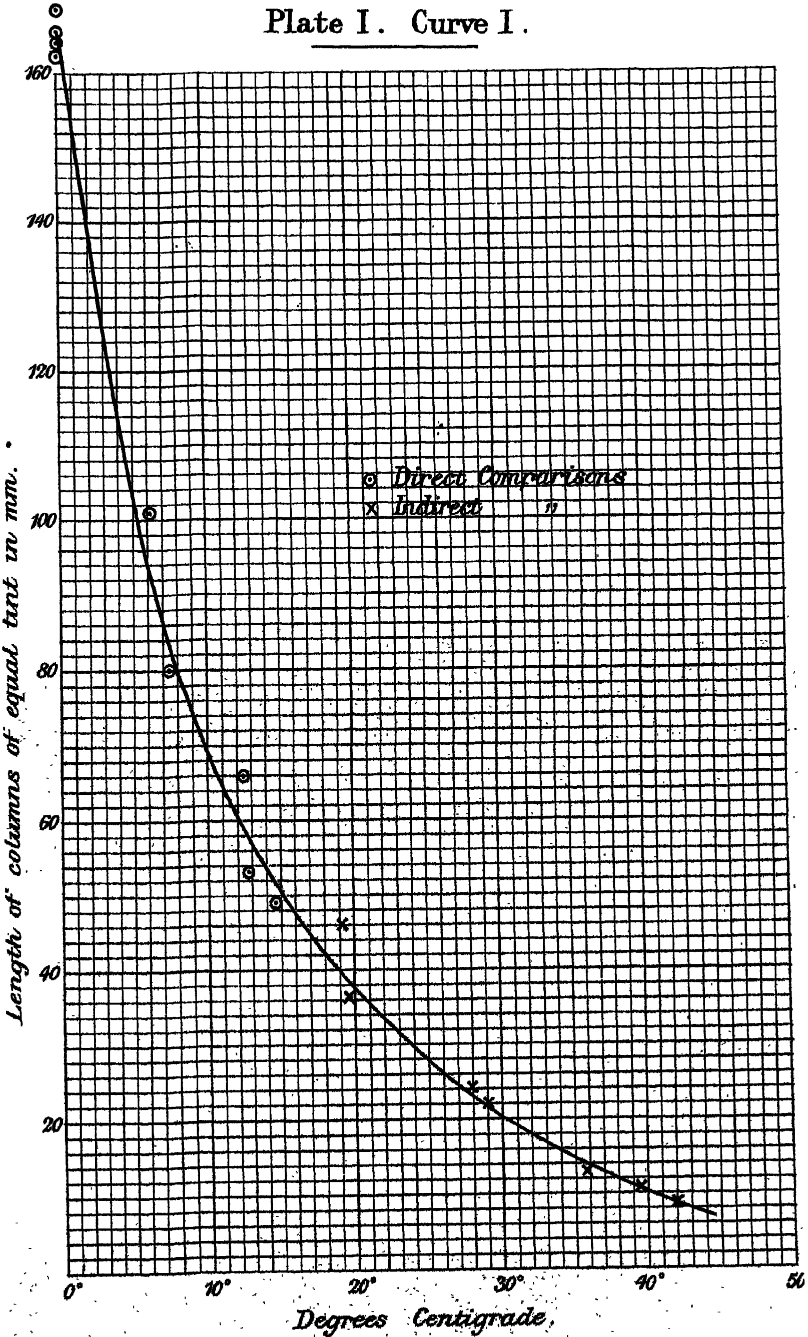
The lengths of the standards at the different temperatures matching 10 mm. of pure peroxide at 0° are plotted as Curve I, Plate I. This is used in the subsequent experiments to find the lengths of the chloroform solutions containing unit amount of NO_2, in order that the relative amount of dissociation in solutions made with other solvents may be referred to the same standard.

The relative dissociation is plotted as Curve II, Plate II.

Solutions in Methylene Chloride.

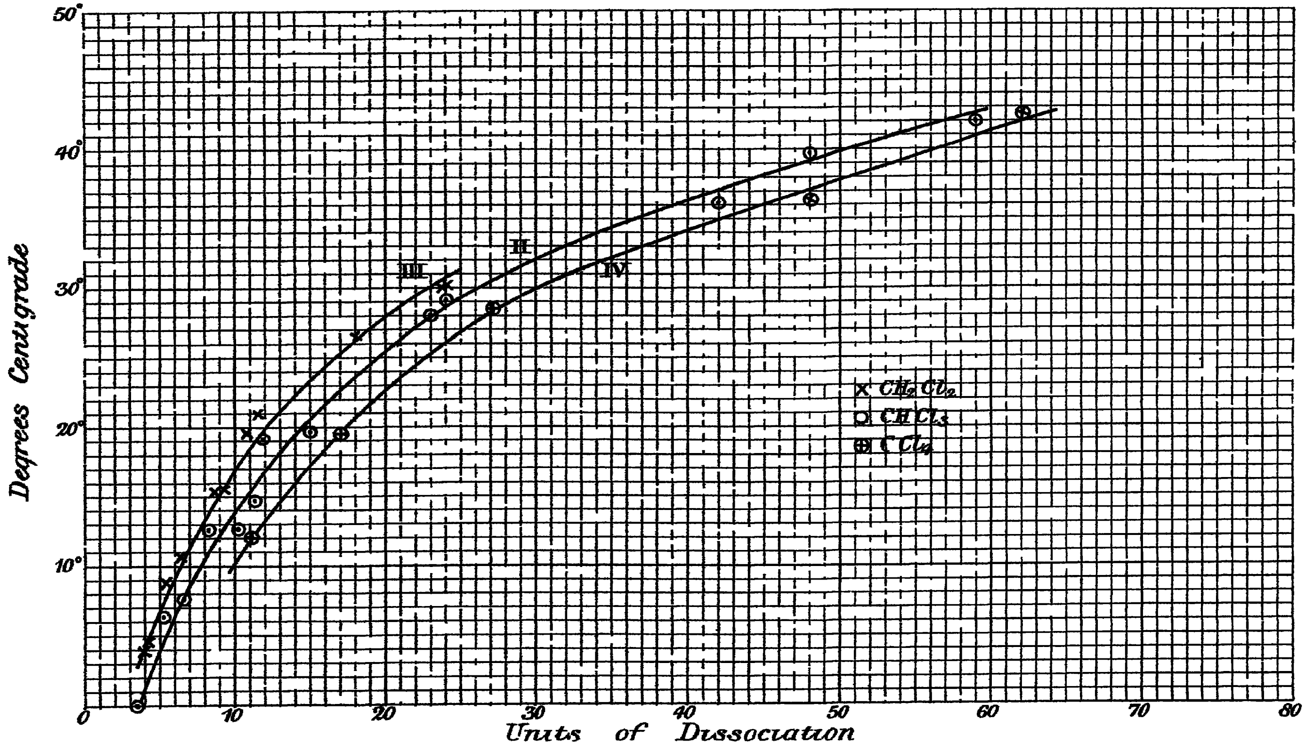
Methylene chloride was prepared by reducing an alcoholic solution of chloroform with zinc dust and dilute hydrochloric acid. The washed distillates from several operations were fractionated, and the portions boiling at 40—43° (uncorr.) mixed with phosphoric anhydride and allowed to stand. The yield was small, and, although several modifications of the process were tried, no better result was

Plate I. Curve I.



Harrison & Sons Lith.
S^t Martins Lane W.C.

Plate II. Curves II–IV



obtained, probably owing to the very volatile methylene chloride being carried off to some extent with the escaping hydrogen.

After standing some days the methylene chloride was poured off from the phosphoric anhydride and distilled. The distillate was made up into solution 1 M, but the colour was not satisfactory, so the solution was agitated out with sodium hydroxide solution, washed with water, dried over phosphoric anhydride, and distilled. Solution 2 M was then made up of 1·82 c.c., or 2·71 grams of nitrogen peroxide in 100 c.c.

The solution was then compared with 1 C, and the results reduced to the standard of 10 mm. of pure peroxide at 0°.

TABLE III.—*Measurement of the Dissociation in Methylene Chloride solution 2 M of* 1·82 *c.c. or* 2·71 *grams per* 100 *c.c.*

Temperature.	Columns 1 C.	Columns 2 M	Length × 1·82	Relative dissociation.
4·3°	110 mm.	130 mm.	237	4·2
10·7	64 "	82 "	149	6·6
15·2	49 "	59 "	107	9·4
19·8	38 "	50 "	91	11·0
26·9	25 "	30 "	55	18·0
30·0	21 "	23 "	42	21·0
4·0	113 "	129 "	235	4·0
4·0	113 "	143 "	260	3·9
8·6	77 "	104 "	189	5·3
15·5	48 "	61 "	111	9·0
21·0	36 "	47 "	86	11·6
4·1	102 "	136 "	248	4·0

The relative dissociation is plotted as Curve III, Plate II

Solution in Carbon Tetrachloride.

Some "chemically pure" carbon tetrachloride* was mixed with phosphoric anhydride, allowed to stand, and distilled. It boiled within a range of 2°, and was divided into three fractions; the middle and major portion, which was of constant boiling point, being used to make up solution 1 T of 1·77 c.c. or 2·64 grams of peroxide to 100 c.c. of solution. The solution was compared with 1 C.

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* Unless otherwise stated, the solvents used were obtained from Messrs. Harrington Brothers, Cork.

TABLE IV.—*Measurement of the Dissociation in Carbon Tetrachloride solution, 1 T, of 1·77 c.c. or 2·64 grams per 100 c.c.*

Temperature.	Columns 1 C.	Columns 1 T.	Length × 1·77	Relative dissociation.
12·0°	61·0 mm.	52 mm.	92	11
19·2	39·5 „	34 „	60	17
28·1	24·0 „	21 „	37	27
36·1	14·0 „	12 „	21	48
42·5	9·8 „	9 „	16	62

The relative dissociation is plotted as Curve IV, Plate II.

Solutions in Ethylene Chloride.

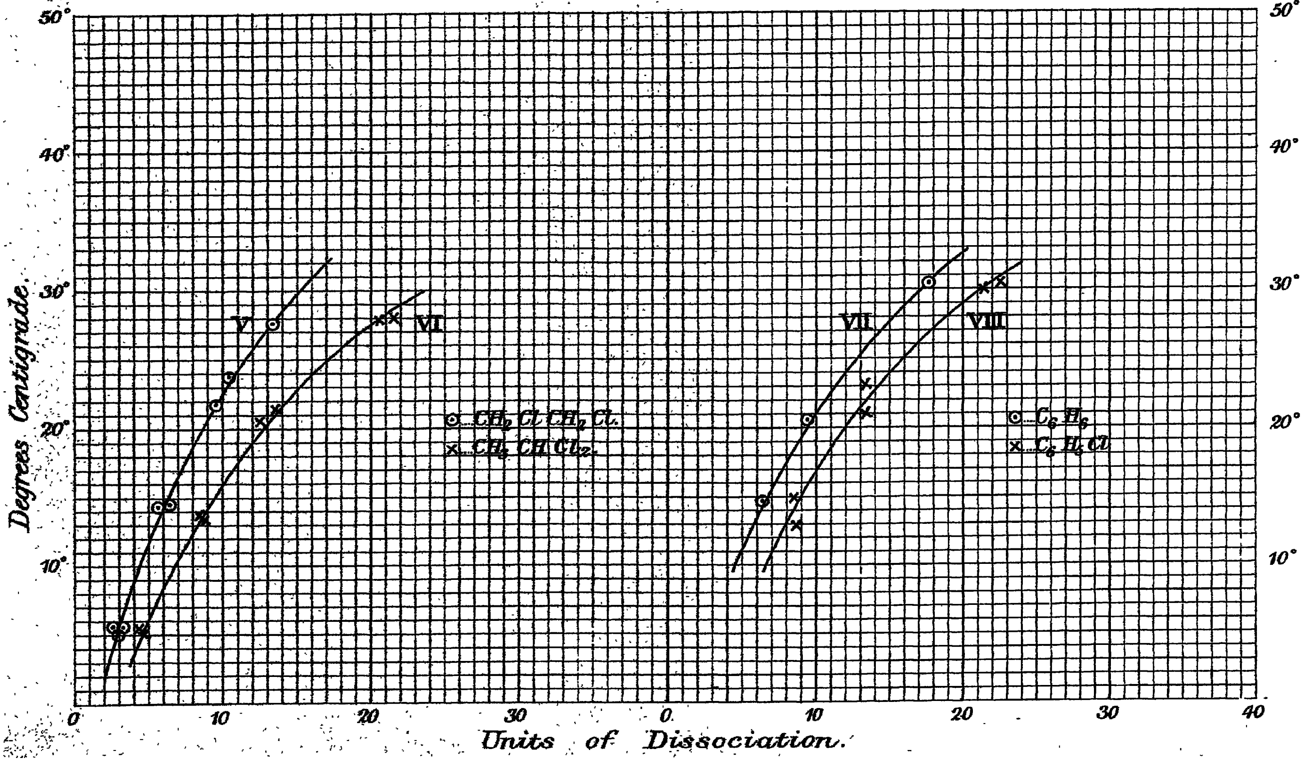
Two hundred and twenty grams of "pure" ethylene chloride was washed, dried, and distilled. The greater portion (b. p. 83—85°) was mixed with phosphoric anhydride, and, after standing, fractionated. The portion boiling from 83·7—84·0° was made up into solution 1 H of 1·79 c.c., or 2·67 grams of peroxide in 100 c.c., whilst from the next fraction (b. p. 84·0—85·1°) solution 2 H of 1·83 c.c., or 2·73 grams in 100 c.c. was prepared. Both solutions were compared with 3 C′.

TABLE V.—*Measurement of Dissociation in Ethylene Chloride solution, 1 H, of 1·79 c.c. or 2·67 grams of Peroxide per 100 c.c., and 2 H of 1·83 c.c. or 2·73 grams per 100 c.c.*

Temperature.	Columns 3 C′.	Columns 1 H.	Length × 1·79.	Relative dissociation.
5·2°	102 mm.	210 mm.	376	2·7
14·2	52 „	96 „	172	5·8
21·9	34 „	58 „	103	9·7
27·8	24 „	42 „	75	13·3
5·5	99 „	184 „	329	3·0
		Columns 2 H.	Length × 1·83.	
5·0°	104 mm.	188 mm.	344	2·9
14·4	52 „	85 „	156	6·4
23·8	30 „	52 „	95	10·5

The relative dissociation is plotted as Curve V, Plate III.

Plate III. Curves V-VIII.



Solutions in Ethylidene Chloride.

A specimen of "pure" ethylidene chloride was washed and fractionated, when almost all passed over between 57·5—58·0° (775 mm.). After standing with phosphoric anhydride, it was poured off, distilled into the weighing flask (b. p. 57·9—58·0° at 779 mm.), and made up into solution 1 Y of 1·97 c.c., or 2·94 grams of peroxide in 100 c.c. After comparison, the solution was emptied out, treated with sodium hydroxide, washed, dried, distilled, and made up into solution 2 Y of 1·79 c.c., or 2·67 grams in 100 c.c. Both solutions were compared with 3 C′.

TABLE VI.—*Measurement of Dissociation in Ethylidene Chloride solutions* 1 *Y of* 1·97 *c.c. or* 2·94 *grams of Peroxide per* 100 *c.c. and* 2 *Y of* 1·79 *c.c. or* 2·67 *grams per* 100 *c.c.*

Temperature.	Columns 3 C′.	Columns 1 Y.	Length × 1·97.	Relative dissociation.
5·4°	100 mm.	113 mm.	223	4·5
13·5	54 „	59 „	116	8·7
20·6	37 „	40 „	79	12·6
25·0	24 „	25 „	49	21·5
		Columns 2 Y.	Length × 1·79.	
5·2°	102 mm.	119 mm.	213	4·7
13·6	54 „	64 „	115	8·7
21·5	35 „	44 „	72	13·9
27·9	24 „	27 „	48	20·8

The relative dissociation is plotted as Curve VI, Plate III.

Solution in Benzene.

Some benzene that had been freed from thiophen by shaking out with sulphuric acid, and purified by fractionation and freezing, was dried by standing over phosphoric anhydride for some weeks. It was then distilled, and a portion was made up into a solution 1 N, but the colour was not good, so the whole of the purified benzene was treated with nitrogen peroxide, shaken out with sodium hydroxide, washed, and dried. A portion was then distilled off (b. p. 79·5—79·9° uncorr.) and made up into solution 2 N of 1·86 c.c., or 2·77 grams of peroxide in 100 c.c. The colour was now quite satisfactory, and the solution was compared with 3 C.

TABLE VII.—*Measurement of Dissociation in Benzene solution, 2 N, of 1·86 c.c. or 2·77 grams of Peroxide per 100 c.c.*

Temperature.	Columns 3 C	Columns 2 N.	Length × 1·86.	Relative dissociation
14·7° 20·6 30·8	32 mm. 37 „ 20 „	84 mm 58 „ 30 „	156 108 56	6·1 9·3 17·9

The relative dissociation is plotted as Curve VII, Plate III.

Solutions in Monochlorobenzene.

"Pure" monochlorobenzene was dried with phosphoric anhydride, and distilled (b. p. 132—133·3°); a middle portion being made up into solution 1 Z of 1·81 c.c., or 2·70 grams in 100 c.c. of solution. Another portion was dried for several weeks over phosphorus pentoxide, distilled and made up into solution 2 Z of 1·98 c.c., or 2·95 grams in 100 c.c. Both solutions were compared with 3 C.

TABLE VIII.—*Measurement of Dissociation in Monochlorobenzene solution, 1 Z, of 1·81 c c. or 2·70 grams of Peroxide, and 2 Z of 1·95 c c. or 2·95 grams per 100 c.c.*

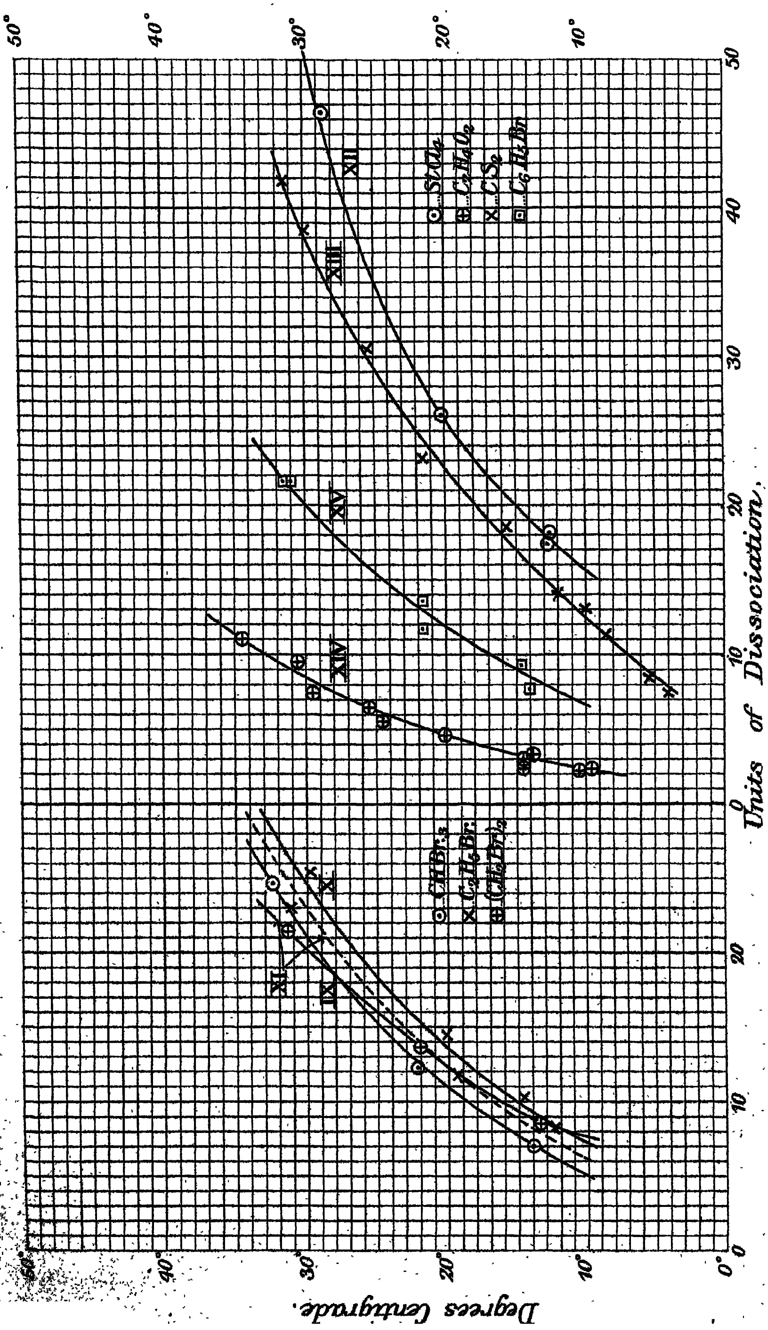
Temperature.	Columns 3 C.	Columns 1 Z.	Length × 1·81.	Relative dissociation
12·8° 21·0 30·0	57 mm 36 „ 21 „	63 mm. 41 „ 26 „	114 74 47	8·5 15·5 21·3
		Columns 2 Z.	Length × 1·95.	
14·9° 23·0 30·5	50 mm. 32 „ 20 „	60 mm. 38 „ 22 „	119 76 44	8·4 13·2 22·7

The relative dissociation is plotted as Curve VIII, Plate III.

Solutions in Monobromobenzene.

Monobromobenzene was prepared by heating purified benzene with bromine and a trace of iodine in a flask fitted with a reflux condenser, until action ceased. The product was washed with sodium hydroxide solution, and with water, dried, and fractionated. The

Plate IV. Curves IX-XV.



portion boiling at 157—158° (uncorr.) was dried with phosphoric anhydride, distilled into the weighing flask, and made up into solution 1 R. The colour of the solution was not quite satisfactory, so it was treated with sodium hydroxide, washed, dried, and distilled, and made up into solution 2 R of 1·92 c.c., or 2·86 grams in 100 c.c. After comparison, the solvent was again purified as before, and made up into solution 3 R, with a new sample of nitrogen peroxide. 3 R contained 1·85 c.c., or 2·76 grams per 100 c.c. Both solutions were compared with 3 C.

TABLE IX.—*Measurement of Dissociation in Monobromobenzene solution, 2 R, of* 1·92 *c.c. or* 2·86 *grams of Peroxide, and* 3 *R of* 1·85 *c.c. or* 2·76 *grams per* 100 *c.c.*

Temperature.	Columns 3 C.	Columns 2 R.	Length × 1·92.	Relative dissociation.
11·5°	51 mm.	56 mm.	108	9·3
21·5	31 „	39 „	73	13·7
31·5	19 „	21 „	40	21·7
		Columns 3 R.	Length × 1·85.	
14·0°	53 mm.	70 mm.	130	7·6
21·5	35 „	46 „	85	11·8
31·0	19 „	25 „	46	21·7

The relative dissociation is plotted as Curve XV, Plate IV.

Solutions in Bromoform.

A specimen of bromoform "puriss" was shaken with sodium hydroxide solution, washed, dried, and distilled. The fraction distilling at 147—149°, was slightly coloured, owing to the decomposi-

TABLE X.—*Measurement of Dissociation in Bromoform solution,* 3 *B, of* 1·82 *c.c. or* 2·71 *grams of Peroxide per* 100 *c.c.*

Temperature.	Columns 3 C.	Columns 3 B.	Length × 1·82.	Relative dissociation.
14·0°	53 mm.	78 mm.	142	7·0
22·1	34 „	44 „	80	12·5
32·4	17 „	22 „	40	25·0

The relative dissociation is plotted as Curve IX, Plate IV.

tion which takes place on distillation under atmospheric pressure To avoid this difficulty, the liquid, after standing with phosphoric anhydride, was distilled under a pressure of 30 mm., when, after the first few cubic centimetres, it came over quite clear and colourless Solution 3 B* was made up from it of 1·82 c.c., or 2·71 grams in 100 c.c. It was compared with 3 C.

Solutions in Ethylic Bromide.

Ethylic bromide, prepared by the action of bromine and red phosphorus on absolute alcohol, was washed with sodium hydroxide solution and water, then dried and fractionated. The portion boiling at 38—39°, was dried with phosphorus pentoxide and distilled; the fraction boiling from 38·1 to 38·3° being made up into solution 2 E of 2·07 c.c., or 3·09 grams per 100 c.c. After comparison, as the colour was not perfect, it was treated with sodium hydroxide solution, washed with water, and dried for some weeks over phosphoric anhydride. It was then distilled (b. p. 37·8—38·1°) and made up into solution 4 E of 1·84 c.c., or 2·74 grams in 100 c.c. Both solutions were compared with 3 C.

TABLE XI.—*Measurement of Dissociation in Ethylic Bromide solutions, 2 E, of* 2·07 *c.c. or* 3·09 *grams of Peroxide per* 100 *c.c., and* 4 *E of* 1·84 *c.c. or* 2·74 *grams per* 100 *c.c.*

Temperature.	Columns 3 C.	Columns 3 E.	Length × 2·07.	Relative dissociation.
12·4°	58 mm	58 mm.	120	8·3
19·6	39 "	41 "	85	11·8
31·3	19 "	21 "	43	23·3
		Columns 4 E.	Length × 1·84.	
14·7°	52 mm.	54 mm.	99	10·1
20·2	37 "	38 "	70	14·3
30·0	21 "	21 "	39	25·6

The relative dissociation is plotted as Curve X, Plate IV.

Solution in Ethylene Bromide.

"Pure" ethylene dibromide was distilled, when, after a very small quantity had come over, practically all the rest boiled at 132·7—132·9°. The latter was mixed with phosphoric anhydride, and after standing, poured off and distilled into the weighing flask, where it was made up into solution 1 O of 1·85 c.c., or 2·76 grams in 100 c.c. The ethylene bromide is measured at 15°, as it solidifies above 0°, and the solution was compared with 3 C.

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* Solutions 1 and 2 B were lost.

TABLE XII.—*Measurement of Dissociation in Ethylene Bromide solution* 1 O *of* 1·85 *c.c. or* 2·76 *grams per* 100 *c.c.*

Temperature.	Columns 3 C.	Columns 1 O.	Length × 1·85.	Relative dissociation.
13·5°	54 mm.	62 mm.	114	8·8
22·2	33 „	41 „	75	13·3
31·6	19 „	25 „	46	21·7

The relative dissociation is plotted as Curve XI, Plate IV. It will be noticed that this curve cuts the others, a thing which happens in no other case. The difference is probably due to slow decomposition, which, if eliminated, would probably give the curve more the position of the dotted one. None of the compounds containing bromine were entirely satisfactory, except perhaps monobromobenzene, as the solutions did not keep well, even after repeated purification.

Solutions in Silicon Tetrachloride.

A perfectly clear and colourless specimen of silicon tetrachloride (specially prepared for me by Messrs. Harrington Brothers), was made up into solution 1 L of 1·85 c.c., or 2·75 grams of peroxide in 100 c.c. of solution. It was compared with 3 C.

It is unfortunate that this solvent is somewhat troublesome to work with, for, in addition to the fact that the solutions keep for an unlimited period quite unchanged, it is probable that nitrogen peroxide is more dissociated in them than in those of any other solvent yet examined.

TABLE XIII.—*Measurement of Dissociation in Silicon Tetrachloride solution,* 1 *L, of* 1·85 *c.c. or* 2·76 *grams of Peroxide per* 100 *c.c.*

Temperature.	Columns 3 C.	Columns 1 L.	Length × 1·85	Relative dissociation.
12·3°	58 mm.	30 mm.	56	18·0
12·5	58 „	31 „	57	17·6
20·0	38 „	21 „	38	25·9
28·5	23 „	12 „	22	46·3

The relative dissociation is plotted as Curve XII, Plate IV.

Solutions in Carbon Bisulphide.

About 800 c.c. of a very pure specimen of carbon bisulphide, which did not react with nitrogen peroxide, was shaken with mercury for some time, filtered into a dry bottle, and allowed to stand over night with phosphoric anhydride; it was then poured off and distilled from a water bath. It boiled constantly at 43·5° (uncorr.). The middle portion of the distillate was collected apart, and with it, solution 1 S was prepared of 1·93 c.c., or 2·88 grams of peroxide to 100 c.c. of solution.

When this solution was compared with 1 C, very discordant figures were at first obtained, until it was discovered that the nitrogen peroxide did not reach its state of equilibrium in carbon bisulphide solution *when cooled*, until some time had elapsed. No such lag was observed when the temperature was raised, or in the other solvents, although it was carefully looked for.

In the results recorded, the readings were only taken after the solution had stood some time at each temperature.

TABLE XIV.—*Measurement of Dissociation in Carbon Bisulphide solution*, 1 *S*, *of* 1·93 *c.c. or* 2·88 *grams of Peroxide to* 100 *c.c.*

Temperature.	Columns 1 C.	Columns 1 S.	Length × 1·93.	Relative dissociation.
3·5°	118·0 mm.	79 mm.	151	6·6
3·9	113·0 „	74 „	142	7·0
3·9	113·0 „	71 „	135	7·4
4·2	111 0 „	71 „	135	7·4
5·2	102·0 „	61 „	116	8·6
5·2	102·0 „	63 „	120	8·4
8·3	78·0 „	47 „	89	11·0
9·5	70·0 „	44 „	84	12·0
9·6	70·0 „	42 „	80	13·0
10·2	67·0 „	39 „	74	13·0
10·6	65·0 „	37 „	70	14·0
12·0	59·0 „	38 „	72	14·0
15·6	48·0 „	28 „	53	19·0
16·0	47·0 „	29 „	55	18·0
21·6	34·5 „	23 „	44	23·0
25·2	28·0 „	18 „	34	30·0
25·4	27·5 „	17 „	32	31·0
29·7	21·0 „	14 „	27	37·0
30·3	20·5 „	13 „	25	40 0
31·1	19·5 „	13 „	25	40·0
31·4	19·0 „	12 „	23	43·0

The relative dissociation is plotted as Curve XIII, Plate IV; closely agreeing determinations being marked as one point.

Solutions in Acetic acid

About 750 c.c. of "glacial" acetic acid, that had been crystallised and separated from the mother liquor repeatedly, was melted and distilled. After a small portion had come over, the boiling point remained at 117° (uncorr.) until nearly all had distilled, when the flame was removed. The middle portion was tested with nitrogen peroxide, but reacted with it. It was consequently redistilled, but it was found to be impossible, by mere fractionation, to get a sufficient quantity absolutely free from water. The stock was then shaken with a *small* quantity of phosphoric anhydride, allowed to stand over-night, poured off, and distilled. It boiled constantly at 117·5° (uncorr.), and was collected apart until it ceased to react with nitrogen peroxide. The operation was repeated, and the product made up into solution 1 A of 1·77 c.c., or 2·64 grams of peroxide to 100 c.c. of solution, the acetic acid being measured at 12·0°.

A second supply of the solvent was prepared in an exactly similar manner from a different stock of acetic acid, and with it solution 3 A was made of 1·90 c.c., or 2·83 grams to 100 c.c.

The solution did not keep well, probably decomposing,—as some experiments, in which the purified acetic acid was heated with nitrogen peroxide in sealed tubes went to show,—according to the equation $2C_2H_3O{\cdot}OH + 3NO_2 = (C_2H_3O)_2O + 2HNO_2 + NO$.

The comparison was made with 1 C.

TABLE XV.—*Measurement of Dissociation in Acetic Acid solution,* 1 *A, of* 1·77 *c.c. or* 2·64 *grams, and* 2 *A of* 1·90 *c.c. or* 2·83 *grams of Peroxide to* 100 *c.c.*

Temperature.	Columns 1 C.	Columns 1 A.	Length × 1·77.	Relative dissociation.
14·5°	52 mm.	181 mm	320	3·1
14·1	53 "	173 "	306	3·3
20·1	28 "	120 "	212	4·7
25·6	27 "	85 "	151	6·6
30·6	20 "	58 "	103	9·7
		Columns 3 A.	Length × 1·90	
9·7°	69 mm	256 mm.	186	2·1
14·6	52 "	187 "	355	2·8
19·4	39 "	135 "	257	3·9
24·7	29 "	92 "	175	5·7
29·7	21 "	69 "	131	7·6
34·6	16 "	47 "	89	11·0
10·2	67 "	251 "	477	2·1

The relative dissociation is plotted as Curve XIV, Plate IV.

Discussion of Results.

Owing to several of the dissociation curves falling so close to each other, it is impossible to draw them all on one sheet without confusion, unless the scale is made very large. In order to remove this difficulty and simplify comparison, the dissociation in the various solvents at the even temperatures 10°, 20°, and 30° was read off the curves, and is stated in Table XVII.

It will be seen that it varies considerably even in solvents of similar composition, increasing with the number of atoms, but not being proportional to the molecular weight. Thus additional carbon atoms are far less effective than hydrogen atoms, and though bromine is more effective than hydrogen it is less so than chlorine. The variation seemed so regular that the values of H, C, and Cl at 20° were calculated from three solvents, and applied to the others containing these elements.

The value for Br cannot be fixed so satisfactorily, as the best solvent containing it has only one atom.

The values for Si and S are unconfirmed, and are found by difference.

The values of H, C, Cl, Br at the other two temperatures are found by altering the values at 20° in the same proportion that chloroform alters under these conditions.

The values of the atoms are given in Table XVI.

TABLE XVI.

Atom.	Dissociation power at 10°.	Dissociation power at 20°.	Dissociation power at 30°.
H	0·67	1·30	2·38
C	0·10	0·20	0·37
Cl	2·25	4·33	7·9
Br	1·77	3·60	6·5
Si	6·70	8·70	20·4
S	5·60	11·20	19·0

The molecular dissociating powers calculated from the values are stated opposite the observed results in Table XVII.

Taking the compounds containing hydrogen, carbon, and chlorine it will be seen that although there is a wide range in the number of the three kinds of atoms in the different solvents, yet the agreement between the calculated and observed values is fairly close. The discrepancy is, in fact, within the limit of experimental error, except in the case of ethylene chloride, where it is so great that I thought it

TABLE XVII.

Solvent.	Dissociation at 10°.		Dissociation at 20°.		Dissociation at 30°.	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
$CHCl_3$	7·7	7·5	14·5	14·5	26·2	26·5
CH_2Cl_2	6·2	6·0	12·0	11·5	22·7	21·0
CCl_4	9·9	9·1	17·5	17·5	30·5	33·0
$CH_2Cl{\cdot}CH_2Cl$....	4·2	7·4	8·7	14·3	15·0	26·1
$CH_3{\cdot}CHCl_2$	6·9	7·4	12·8	14·3	23·2	26·1
C_6H_6	4·6	4·6	9·2	9·0	17·0	16·5
C_6H_5Cl	6·5	6·2	12·0	12·1	21·2	22·0
C_6H_5Br	6·7	6·7	11·7	11·3	20·0	20·6
$CHBr_3$..........	5·0	6·1	11·0	12·3	21·0	22·3
C_2H_5Br	7·0	3·8	13·5	10·5	24·5	19·1
$CH_2Br{\cdot}CH_2Br$ ...	7·8	6·4	12·5	12·8	20·3	23·3
$SiCl_4$	15·7	—	26·0	—	52·0	—
CS_2	12·2	—	22·5	—	38·3	—
$C_2H_3O{\cdot}OH$......	2·3	—	4·6	—	8·5	—

worth while to make a determination of the molecular weight of both ethylene and ethylidene chlorides by measuring the depression of the freezing point of their acetic acid solutions. The molecular weights found were 102 and 103 respectively; the calculated being 99.

Though the states of aggregation of these compounds may be very different in dilute acetic acid solution from what it is when nearly pure, yet it seems probable from the facts, that the "dissociating power" of a solvent is not merely additive, but also constitutive. The behaviour of acetic acid, in this respect, points to the same conclusion, for otherwise O would have a negative value. Solvents containing bromine, as might be expected from the fact that they are by no means unexceptionable in their behaviour towards nitrogen peroxide, give results which do not agree so closely with the calculated values.

The varying dissociating power of solvents towards nitrogen peroxide resembles the result obtained by Menschutkin. Indeed, in his experiments on the rate of etherification of alcohols (*Zeit. physikal. Chem.*, 1888, 1, 611), the ratio of the rates in benzene, xylene, and hexane is very nearly the same as that of the dissociating powers as calculated from my constants (Table XVIII).

In his further experiments on the interaction of triethylamine and ethylic iodide, the results are, however, quite different; in fact, increase in complexity, as a rule, diminishes the rate.

It is, however, obvious that my experiments, as well as Menschutkin's show that the so-called "indifferent solvent" has a

TABLE XVIII.

Solvent.	Etherification rate of isobutyl alcohol.	Etherification rate of isopropyl alcohol.	Dissociating power.
Benzene	1·00	1·00	1·0
Xylene	1·37	1·25	1·6
Hexane	2·16	2·07	2·2

specific action on the dissolved substance, possibly similar to that which causes the change in the state of molecular aggregation of acetic acid when dissolved in benzene, in ether, and in water.

In order to test the suggestion, made by Menschutkin, that this kind of influence belongs to a low order of chemical action, the following experiments were made. Twenty cubic centimetres of chloroform were placed in the receiver of a Beckmann's freezing-point apparatus, along with a bulb containing a weighed quantity of nitrogen peroxide. The temperature was allowed to become steady, and the bulb smashed, when a rapid fall of temperature took place. Two determinations were made: in the 1st, 0·705 gram of peroxide was mixed with 30·6 grams of chloroform, when the temperature fell 0·34° (to 15·0° C.); and in the second, 0·676 gram added to 30·6 grams produced a fall of 0·34° (to 15·7° C.). Similar measurements were then made with carbon tetrachloride. In the 1st, 0·668 gram of peroxide was added to 32·6 grams of carbon tetrachloride, and gave a fall of 0·60° (to 15·4° C.); whilst in the 2nd, 0·652 gram added to 32·6 grams gave a fall of 0·63° (to 15·7° C.).

Calculating the mean heat absorbed in the case of the chloroform, we have it equal to 30·6 grams × 0·34° × 0·233 (sp. ht. of $CHCl_3$) + 0·69 gram × 0·34° × 0·46 (sp. ht. of N_2O_4) + 1·8 gram (the water equivalent of apparatus immersed) × 0·34° = 3·1 cal., and in the case of the carbon tetrachloride equal to 32·6 grams × 0·62° × 0·177 (sp. ht. CCl_4) + 0·66 gram × 0·62° × 0·46 + 1·8 gram × 0·62° = 4·8 cal.

The ratio of the heat absorbed in dissolving nitrogen peroxide in chloroform to that in dissolving in carbon tetrachloride is as 3·1 : 4·8 or as 1·00 : 1·55.

Now the ratio between the dissociation in these solvents under the same conditions is as 1·00 : 1·23, showing that the heat absorbed is not proportional to the dissociation measured by the colour.

This difference at first sight suggests that in addition to the heat absorption, some exothermic action has taken place, and has gone farther in the case of chloroform than with carbon tetrachloride;

fitting in excellently with the idea that a sort of compound is formed by the union of nitrogen peroxide and solvent. Now, on calculating the heat of dissociation of liquid nitrogen peroxide, the following result is obtained. The difference between the dissociation at 15° in pure peroxide and a 2·2 per cent. by vol. solution is approximately 10·0 − 3·3 = 6·7 units of dissociation, and the weight of N_2O_4 decomposed is 6·7 × 0·0468 gram in 100 grams, and 6·7 × 0·0468 × 0·007 = 0·0024 gram in the weight taken. On solution, 3·1 cal. was given out, so if the absorption of heat was due only to dissociation, then 3·1 ÷ 0·0024 = 1300 cal. will be absorbed on 1 gram of the peroxide dissociating. Calculating in a similar way for the solutions in carbon tetrachloride it is found that 4·8 ÷ 0·0030 = 1600 cal. as the heat of dissociation for 1 gram.

Van't Hoff (*Etudes*, 133; cited Nernst's *Theor. Chem.*, *Eng. Trans.*, 559) has calculated the heat of dissociation of gaseous nitrogen peroxide from the specific heats of the gas. He finds it to be 136 cal. for 1 gram; an enormously less quantity than that obtained above. Though the heat of dissociation may be different in the gaseous state from what it is in solution, yet this probably negatives the view that any *exothermic* union takes place between the solvent and dissolved substance.

I am at present engaged in the further examination of the question of the heat changes on solution, and have already found that the solution of a small quantity of carbon tetrachloride in chloroform is the probable cause of a distinct lowering of temperature.

I have also made some experiments on the dissociation of solutions in which the concentration of the nitrogen peroxide is comparable with that of the gas, which go to show that the rates of dissociation rapidly approximate, but as some time must elapse before I can pay much attention to the matter, I have ventured to bring forward the present communication.

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LXXXIII.—*Kjeldahl's Method for the Determination of Nitrogen.*

By BERNARD DYER, D.Sc.

KJELDAHL'S method for the determination of nitrogen has, in some one or other of its modifications, superseded the well-known soda-lime process of Varrentrap and Will in most agricultural laboratories, both in England and on the Continent, and to a very large extent in America. For the analysis of feeding stuffs and fertilisers, it has many advantages over the soda-lime process, not being liable to the errors arising from variations of temperature in combustion, and obviating the necessity for reducing the substance to the fine state of division required when that method is used.

Kjeldahl's process, as originally devised, had the disadvantage of being very slow, but the modification introduced by Gunning has not only rendered it speedy, but also increased the accuracy, whilst Jodlbauer's modification has enabled it also to replace the Ruffle process for the determination of total nitrogen in fertilisers containing nitrates as well as organic ammoniacal nitrogen.

The method, however, has not found its way into the laboratory of the organic chemist—at any rate in England—and I determined, with the help of one of my assistants, Mr. E. H. Roberts, to try it on a number of representative organic compounds of varied constitution.*

It will be convenient at the outset to describe the particular modifications of the process which experience has led me to adopt.

The original Kjeldahl process consisted in the oxidation of the substance by boiling with strong sulphuric acid, completing the action by the addition of potassium permanganate (*Zeit. Anal. Chem.*, **22**, 366). The use of potassium permanganate cannot be recommended, unless the quantity used is very moderate; it has a tendency to cause low results, probably by oxidizing the ammonia. On the other hand, however, the use of a drop of mercury, or a little mercuric oxide (Wilfarth, *Chem. Centr.*, 3, 16, 17, 113; and Arnold *loc. cit.*, 337) is a great advantage, as it greatly expedites the oxidation of carbonaceous matter. The greatest advance made on the process, however, was the introduction by Gunning (*Zeit. Anal. Chem.*, **28**, 188) of the use of potassium sulphate as an addition to the sulphuric acid after the action of the acid on the material had continued for a short time. This reduced the time of oxidation in the case of refractory substances from some hours to about half an hour, or even less. The effect is to form a strong acid solution of potassium bisulphate, which boils at a considerably higher temperature than the sulphuric acid, thereby very greatly facilitating the oxidation. When the Gunning modification is employed, the use of mercury can be dispensed with; although a little mercury renders the process even still more rapid. This process with the addition of mercury, which I now describe, I shall refer to as the "Kjeldahl-Gunning-Arnold" process.

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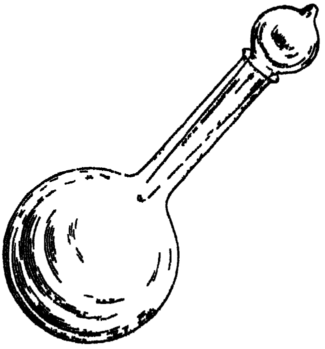
* At the time these experiments were undertaken, the author was unaware of the work of Dafert (*Landwirth-Versuchs.*, **34**), and of the later work of Arnold and Wedermeyer (*Zeit. Anal. Chem.*, **31**, 525) in the same direction. On the whole, the experience of these authors is similar in most directions to that now recorded, although the majority of the representative compounds selected for their experiments were different from those used by the present author.

In the analysis of feeding stuffs or fertilisers (not containing nitrates), any quantity, varying according to circumstances, from 0·5 gram to 5 grams, or even more, is introduced into a round-bottomed flask of hard Jena glass, and treated with about 20 c.c. of strong sulphuric acid, with the addition of a single drop of mercury. The flask is closed with a loosely fitting balloon stopper (*see* Fig.), and heated over a gas flame, gently at first, until the initial vigorous action has ceased; the heat is then gradually increased, so that the liquid boils briskly, and in about 15 minutes 10 grams of potassium sulphate are added, and the boiling continued until the contents of the flask are clear and colourless; this generally occurs within about half an hour, or, in the case of very carbonaceous substances, within an hour. The sulphuric acid condenses on the internal projection of the balloon stopper, and falls back, so that there is little loss of acid except as sulphurous acid. The contents of the digesting flask are then washed out into a spacious distilling flask, also of Jena glass, which is connected by a doubly perforated cork with any convenient condensing apparatus; the second perforation bearing a tapped funnel through which an excess of sodium hydrate solution is added, and also a little sodium sulphide to decompose any nitrogen compounds of mercury that may be formed; if mercury is not used, the sodium sulphide may of course be dispensed with. Some zinc foil is put in the flask to prevent bumping, and the products of distillation are collected in a measured quantity of standard acid, the ammonia which distils over being determined by titration in the usual way. I find it best to allow the steam charged with ammonia to pass directly into the acid, contained in a flask standing in a tank of running water, using as a means of communication between the distilling flask and the receiving flask a block-tin tube bent in the form of an arch; this rises perpendicularly from the cork of the distilling flask to a height of 15 or 18 inches before turning over. With the apparatus arranged in this way, I find that there is no danger whatever of the passing over of soda spray with the steam, and the use of any of the various forms of "spray trap" is unnecessary. The other end



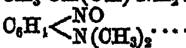
of the tube is united by a cork to a pear-shaped adapter having a large expansion, and terminating in a narrow end which dips into an ordinary Erlemeyer flask in which the acid is contained. The pear-shaped expansion allows for the variations of pressure during distillation, and is sufficient to avoid any regurgitation of the acid into the distilling flask.

There is but little difficulty in obtaining sulphuric acid, sodium hydroxide, and sodium sulphide practically free from nitrogen compounds, or so free as to introduce practically no error into the determination. A blank experiment should, however, always be made when new stocks of material are bought, and the result, including the slight error caused by the action of steam or standard acid on the glass, should not give an error (constant for the particular materials in use) amounting to more than the equivalent of 0·0003 to 0·0005 gram of nitrogen, or from 0·2 c.c. to 0·4 c.c. of decinormal sodium hydroxide solution. The smaller margin of alkalinity will generally be reached in the distillate, even when distilled water is boiled over. In my own laboratory, the error is determined as a matter of routine at least once a week, but it is rare to find it exceeding the higher limit of 0·0005 gram.

When nitrates are present in addition to organic or ammoniacal nitrogen, Jodlbauer's modification (*Chem. Centr.*, 3, 17, 433) suffices to determine accurately the total nitrogen. This process consists in previously adding to the sulphuric acid used for oxidation, either phenol or, preferably, salicylic acid—generally about 2 grams for a determination. While the contents of the flask are still cold, from 1 to 2 grams of zinc dust are added (as well as a drop of mercury) and allowed to dissolve before the flask is heated. The process is then continued exactly as before, when the whole of the nitrogen is obtained as ammonia. There is no difficulty whatever in determining the nitrogen in potassium or sodium nitrate in this manner; but I find that when ammonia salts are present as well as potassium or sodium nitrate, the results are invariably too low, unless the sulphuric acid containing the salicylic acid is poured quickly into the flask out of a beaker, so that the nitrate shall be completely covered by the acid before the lapse of an appreciable interval of time; this prevents the formation of the lower oxides of nitrogen, and consequent loss. When even ammonium nitrate is treated in this way, the whole of the nitrogen is retained in solution. I allude to this detail, because I have nowhere seen attention drawn to it, and because I think there is a probability of large errors occurring in the analysis of compound fertilisers, including mixtures of ammonia salts and alkali nitrates, if the acid is allowed to flow on to the sample from a pipette in the usual way. I have little doubt that the observance of the simple precaution mentioned above will remove a difficulty which has hitherto been productive of discrepancies in the analysis of such materials. The process, as I have described it, may be called the Kjeldahl-Gunning-Arnold-Jodlbauer process.

The degree of accuracy possessed by these methods will be to some extent gathered from the results of their application to the various compounds now to be mentioned. It should be said that in calculating the percentages of nitrogen the atomic weights used are O = 16; C = 12; N = 14·046; H = 1·0024; S = 32·06. The strengths of the standard solutions of acid and of alkali used in titrating, were determined by reference to pure ammonium sulphate.

Kjeldahl-Gunning-Arnold Method.

Compound.	Formula.	Percentage of nitrogen calculated.	Percentage of nitrogen found.
Uric acid	$C_5H_4N_4O_3$	33·40	33·31, 33·31
Asparagine	$C_2H_3(NH_2)\cdot(CO\cdot NH_2)(CO\cdot OH)$	18·71	18·69, 18·69
Caffeïne	$C_8H_{10}N_4O_2$	28·93	28·94
Indigotin	$C_{16}H_{10}N_2O_2$	10·72	10·57, 10·51
Atropine	$C_{17}H_{23}NO_3$	4·86	4·83
Morphine (anhyd.)	$C_{17}H_{19}NO_3$	4·63	4·58, 4·62
Quinine sulphate (anhydrous)	$(C_{20}H_{21}N_2O_2)_2H_2SO_4$	7·53	7·54
Strychnine	$C_{21}H_{19}N_2O_4$	8·41	8·39, 8·42
Aniline	$C_6H_5\cdot NH_2$	15·09	14·95, 14·95
Sulphanilic acid (para-amidobenzenesulphonic acid)	$C_6H_4\cdot NH_2\cdot SO_3H$	8·11	8·08, 8·09
Diphenylamine	$(C_6H_5)_2NH$	8·31	8·33, 8·33
β-Naphthylamine	$C_{10}H_7NH_2$	9·82	9·83, 9·84
Acetanilide	$C_6H_5\cdot NH\cdot C_2H_3O$	10·40	10·42
Orthobenzoic sulphinide	$C_6H_4{<}{\substack{CO \\ SO_2}}{>}NH$	7·67	7·64
Parasulphamidobenzoic acid	$C_{64}(HSO_2NH_2)\cdot COOH$	6·98	6·97
Pyridine	C_5H_5N	17·77	17·45, 17·48
Benzidine (diamidophenyl)	$C_{12}H_8(NH_2)_2$	15·26	15·24
Aldehyde-ammonia	$CH_3\cdot CH(OH)\cdot NH_2$	23·00	23·03, 23·12
Nitrosodimethylaniline	 $C_6H_4{<}{\substack{NO \\ N(CH_3)_2}}$	18·71	18·52, 18·74, 18·59
Potassium cyanide (? pure)	KCN	21·55	21·27, 21·27
Ethylic cyanide (propionitrile) (? pure)	$C_2H_5\cdot CN$	25·51	25·13, 25·21
Potassium ferrocyanide	$K_4(FeC_6N_6)$	19·93	19·91, 20·00
Potassium ferricyanide*	$K_3(FeC_6N_6)$	25·56	24·84, 24·81, 24·93

* Addition of zinc dust gave nitrogen, 25·26; addition of sodium thiosulphate gave nitrogen, 25·41, 25·42, 25·39, 25·49.

Kjeldahl-Gunning-Arnold Method, Jodlbauer Method, and Modifications.

Compound.	Formula.	Percentage of nitrogen calculated.	Without reducing agent.	With zinc dust.	Salicylic acid and zinc dust.	Sugar and zinc dust.
Azobenzene	$C_6H_5{\cdot}N_2{\cdot}C_6H_5$	15·42	14·94 14·85	15·04 14·91	15·45 15·45	15·46
Amidoazobenzene	$C_6H_5{\cdot}N_2{\cdot}C_6H_4{\cdot}NH_2$	21·37	12·19 10·66	21·28	—	—
Amidoazotoluene	$CH_3{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_3(CH_3){\cdot}NH_2$	18·71	—	18·79	—	—
Carbazol	$NH(C_6H_4)_2$	8·41	8·25 8·29	8·25 8·29	— —	— —
Hydrazobenzene*	$C_6H_5{\cdot}NH{\cdot}NH{\cdot}C_6H_5$	15 25	15·25	—	—	—
Hydroxylamine hydrochloride	$NH_2{\cdot}OH,HCl$	20·21	3·18 1·64	10·61 9·42	18·84 18·84	Salicylic acid, sugar and zinc. 20·24† 20·18 20·21
Acetaldoxime	$CH_3{\cdot}CH{:}NOH$	23·78	23·08 23 00	23·30	—	Sugar and zinc. 23·59
β-Naphthaquinone(α)oxime	$C_{10}H_6O(NOH)$	8·12	8·10 8·11	—	—	—
Sodium nitroprusside‡	$Na_2(NO)(FeC_5N_5),2H_2O$	28·24	20·36	25·76	25·76	26·44

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* Hydrazobenzene, the "symmetrical" diphenylhydrazine, gives the theoretical yield of nitrogen, but phenylhydrazine hydrochloride, $C_6H_5{\cdot}NH{\cdot}NH_2{\cdot}HCl$ (N = 19·43), whether by the Kjeldahl-Gunning-Arnold method (N = 5 57), the Jodlbauer method (N = 8 55), or the latter with the addition of sugar (N = 16·65), failed to give satisfactory results. Hydrazobenzene, however, is rapidly converted on treatment with sulphuric acid into benzidine, which accounts for the good results obtained. Glucosazone, $C_{18}H_{22}O_4N_4$ (N = 15 68), also failed by any of these modifications to give more than 14·24 per cent. of nitrogen.

The direct inapplicability of Kjeldahl's process or its modifications to hydrazines has been already pointed out by Dafert (*Landw. Versuchs.*, 34), who suggests first reducing hydrazine salts with sugar in presence of sodium acetate for some hours before adding sulphuric acid.

† Sugar and zinc, without salicylic acid, gave only N = 18 72 and 18 17.

‡ The sample of nitroprusside was pure and of normal constitution, for a Dumas combustion of it, kindly made for me by Professor Meldola, gave the full theoretical yield of nitrogen.

Kjeldahl-Gunning-Arnold-Jodlbauer Method.

Compound.	Formula.	Percentage of nitrogen calculated.	Percentage of nitrogen found.
Potassium nitrate	KNO_3	13·88	13·81, 13·93, 13·90
Ammonium nitrate	$NH_4{\cdot}NO_3$	35·07	35·08, 35·07, 35·13
Urea nitrate	$CO(NH_2)_2,HNO_3$	34·21	34·14, 34·14
Nitrobenzene*	$C_6H_5{\cdot}NO_2$	11·41	11·38, 11·35
α-Nitronaphthalene	$C_{10}H_7{\cdot}NO_2$	8·12	8·15, 8·15
m-Nitraniline†	$C_6H_4(NO_2){\cdot}NH_2$	20·34	20·21, 20·24, 20·21
Dinitrobenzene	$C_6H_4(NO_2)_2$	16·71	16·54, 16·51
Picric acid (trinitrophenol)‡	$C_6H_2(NO_2)_3{\cdot}OH$	18·39	18·39, 18·39, 18·35
Potassium parabromochloronitrophenol§	$C_6H_2ClBr(NO_2){\cdot}OK$	4·83	4·85

LXXXIV.—*The Colouring and other Principles contained in Chay Root.* Part II.

By A. G. Perkin and J. J. Hummel.

The results of a previous investigation of this dye stuff (Trans., 1893, **63**, 1160) showed that its tinctorial properties were due to the fact that it contained both alizarin and its glucoside, ruberythric acid, and that in this and other respects it bore a somewhat close resemblance to madder. Special interest, however, lay in the fact that it contained over 1 per cent. of a mixture of yellow substances soluble in baryta water, which is a large quantity compared with the amounts of similar products known to exist in madder, mang-koudu (*Morinda umbellata*, Trans., 1894, **65**, 851), and other allied roots.

The isolation of the principal constituents of chay root was effected by four methods, namely, extraction with alcohol, alum solution, dilute sulphurous acid, and lime water. The product thus obtained consisted of cane sugar, chlororubin, ruberythric acid, alizarin, two dimethylic ethers of anthragallol, an alizarin methyl ether, and metahydroxyanthraquinone. In addition to these, there were indications of the presence of at least two other substances, but in quantity too small to admit of their identification, and it seemed evident that this could only be accomplished by the examination of a very large quantity of raw material.

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* Nitrobenzene treated with sulphuric acid, and reduced with zinc dust (without salicylic acid) gave, in two experiments, N 11·09 and 11·38. When salicylic acid also was used, as in the full Jodlbauer method, the more concordant and accurate results above given were obtained.

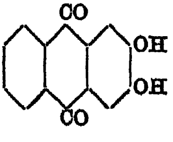
† Zinc reduction only, without the use of salicylic acid, gave nitrogen only 20·06, 20·12, and 20·18.

‡ Zinc reduction only, without salicylic acid, gave nitrogen only, 16·27 and 16·27. The substitution of sugar for salicylic acid gave 17·93 and 17·93—a fact interesting in the light of some subsequent results.

§ Zinc reduction only, without salicylic acid, gave also nitrogen, 4·85.

Application was therefore made to the Imperial Institute, and our thanks are due to the authorities of this Institution, who very readily supplied us with 2 cwts. of the root for further examination. The results now obtained, whilst corroborating those of the former communication, have shown the existence in this dye stuff of two new substances which have been examined and identified. The details of their isolation are given in the experimental portion of this paper.

Substance of the formula $C_{15}H_{10}O_4$.—This was obtained as long, orange-yellow needles, melting at 232°; it sublimes partially at higher temperatures. A characteristic property of this substance, when compared with those accompanying it in chay root, is that its potassium and ammonium derivatives are readily soluble in ethylic or methylic alcohols, but insoluble in cold isobutylic alcohol. They crystallise in fine, garnet-red needles, the ammonium derivative being decomposed on exposure to air with evolution of ammonia. By its reaction with zinc dust in alkaline solution, it appeared to be an anthraquinone or allied compound. When heated with hydrochloric acid at 180°, it yielded a yellow, crystalline colouring matter of the formula $C_{14}H_8O_4$, dissolving in alkalis with a blue-green coloration, and yielding a diacetyl derivative, $C_{14}H_6O_4(C_2H_3O)_2$, which melted at 206°. This substance was found to be identical with the *hystazarin* of Liebermann and Schoeller (*Ber.*, 1888, **21**, 2501),

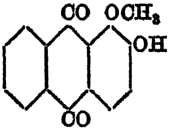


which is obtained, together with alizarin, by the action of phthalic anhydride on catechol in the presence of sulphuric acid. Its dimethylic ether has recently been obtained by heating 3:4-dimethoxyorthobenzoylbenzoic acid with sulphuric acid (Lagodzinski, *Ber.*, 1895, **28**, 116). The first-mentioned authors state that, when heated, hystazarin darkens at 260° without melting. A darkening effect was certainly observed at this temperature, but this was evidently due to the action of the alkali of the glass on a trace of sublimed substance surrounding the product, for, on heating to 316°, it was still unmelted, and on inverting the tube the original product can be recovered with its yellow colour unchanged. Examination by Zeisel's method showed that the substance $C_{15}H_{10}O_4$ contains one methoxy-group, and is therefore *hystazarin monomethyl ether*.

Substance of the formula $C_{16}H_{12}O_5$ (*C*).—This crystallises from alcohol in felted masses of minute needles, melting at 212—213° and soluble in dilute alkalis and ammonia with a crimson colour. Its ammonium derivative is readily soluble in alcohol and in isobutylic alcohol, a point which distinguishes it from the anthragallol dimethyl ether (*A*) melting at 209° and the alizarin methyl ether which accompany it. Like the former, however, its barium derivative is insoluble in dilute alcohol, and the lead compound is insoluble in cold alcohol. It does not dye mordanted calico. When treated with zinc dust, its alkaline solutions become orange, but on exposure to air they regain their original colour, from which it would seem to be an anthraquinone or allied derivative. When heated with sulphuric or hydrochloric acid at 180°, it is converted into anthragallol, and by Zeisel's method it was found to contain two methoxy-groups. Its acetyl derivative was obtained in orange-yellow needles melting at 160°, but the quantity was insufficient for analysis. The substance $C_{16}H_{12}O_5$ (*C*) is therefore an *anthragallol dimethyl ether*, and chay root is thus shown to contain the three possible isomers—

Anthragallol dimethyl ether (*A*)........	M. p.	209°
” ” (*B*)........	”	225—227°
” ” (*C*)........	”	212°
Acetyl compound	M. p.	213—215°
” ”	”	175°
” ”	”	160°

Since the publication of our former communication (*loc. cit.*), Schunck and Marchlewski (Trans., 1894, **65**, 182) have studied the methylation of alizarin, and, as has been shown to be the case with the xanthones, found that it was not possible to obtain an alizarin monomethyl ether containing the methoxy-group in the α-position, whereas the β-compound was readily formed; the latter was not, however, identical with that shown to exist in chay root (*loc. cit.*), which must, therefore, be the α-compound.



The readiness with which this substance is decomposed into alizarin, even by boiling with baryta water, shows that, contrary to the usual nature of these compounds, the methoxy-group in this instance is readily decomposed, and this accounts for its not being produced by the usual methods.

During this investigation, metahydroxyanthraquinone was obtained in larger amount than could be accounted for on the supposition that it had been produced during the decomposition of the ruberythric acid by the boiling lime water, a point previously discussed, and it must therefore be considered to exist as such in the root.

It is probable that those substances which are extracted by means of dilute sulphurous acid are present in the form of glucosides, though it has already been shown that these also exist to some extent in the free state. On the other hand, those which are only obtained by means of lime water, namely, metahydroxyanthraquinone and hystazarin monomethyl ether, are present in the free state only in the root.

EXPERIMENTAL PART.

The extraction of the root was effected as before by means of dilute sulphurous acid and lime water. In consequence of the difficulty of manipulating such large quantities of raw material, this portion of the work was kindly undertaken for us by Messrs. Hirst, Brooke, and Hirst, of Leeds, to whom our best thanks are due. From the "green alizarin" thus obtained, the mixed yellow substances were isolated in the laboratory in the usual manner by extraction with toluene.

Extraction of Chay Root with Lime Water.

The finely-ground, crude product thus obtained was digested as usual for several hours with boiling toluene and filtered. On standing, the filtrate deposited an orange-yellow substance, which was collected apart, a point which was not previously taken advantage of, but which has now been found to be of material advantage in separating the mixed substances. This substance was found to consist entirely of metahydroxyanthraquinone and anthragallol dimethyl ether (*B*), m. p. 225—227°, which could be readily separated, owing to the fact that the former alone yields an ammonium derivative, sparingly soluble in alcohol. In this manner, about 95 per cent. of the metahydroxyanthraquinone contained in the lime water extract can be removed from the mixture, owing to its sparing solubility in toluene. A considerable quantity was thus obtained.

The toluene mother liquors were extracted with dilute alkali, the alkaline solution neutralised with acid, and the yellow precipitate collected, washed, and dried. The product was dissolved in boiling alcohol, and, after cooling the crystalline matter which had deposited, was washed with alcohol and dried. It consisted of two substances, which could be readily separated, owing to the fact that when their solution in hot isobutylic alcohol is treated with ammonia only one is precipitated on cooling in the form of an ammonium derivative; this was collected, washed with isobutylic alcohol, decomposed with acid, and purified by crystallisation from alcohol.

0·1325 gave 0·3452 CO_2 and 0·0468 H_2O. C = 71·05; H = 3·91.
$C_{15}H_{10}O_4$ requires C = 70·86; H = 3·93 per cent.

It appears as a glistening mass of long, orange-yellow needles, sparingly soluble in alcohol; it melts at 232° and sublimes at higher temperatures, undergoing partial decomposition. Dilute alkalis dissolve it, forming crimson coloured solutions, which, when boiled with zinc dust, become brown-orange, regaining their original tint on exposure to air. Like the ammonium derivative, the potassium compound is readily obtained in a crystalline condition by adding alcoholic potash to a solution of the substance in isobutylic alcohol. Both appear as minute, garnet-coloured needles, the former, on exposure to air, being decomposed with evolution of ammonia. The ammonium derivative is readily soluble in ordinary alcohol, a property which distinguishes the substance $C_{15}H_{10}O_4$ from anthragallol dimethyl ether (*A*), melting at 209°, and from alizarin methyl ether. It does not dye with mordants.

Action of Hydrochloric and Sulphuric acids.—As the substance was suspected to contain a methoxy-group, it was heated with fuming hydrochloric acid in a sealed tube at 180° for two hours. After cooling, the tube was found to contain very minute needles, considerably smaller than those of the original substance, and moreover of a decided yellow colour, which distinguished them from those of alizarin or anthragallol, for these, when produced by the decomposition of their methylic ethers in this same way, have always a red-orange tint. The substance was collected and purified by crystallisation from nitrobenzene.

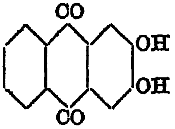
0·1072 gave 0·2749 CO_2 and 0·0350 H_2O. C = 69·93; H = 3·62.
$C_{14}H_8O_4$ requires C = 70; H = 3·33 per cent.

This substance formed a pale yellow mass of minute needles which did not melt below 316°, but when strongly heated, yielded a sublimate, leaving a carbonaceous residue. Dilute alkalis dissolved it with a blue-green coloration, and these solutions when treated with lime or baryta water, yielded violet, insoluble precipitates. It dyes mordanted calico with difficulty, giving pale shades similar to but somewhat redder than those obtained with anthragallol. In order to convert it into its acetyl derivative, it was boiled with acetic anhydride for three hours. The solution obtained was treated with a little alcohol, and the crystalline mass deposited on cooling, collected and purified by crystallisation from alcohol. On analysis the following numbers were obtained.

0·1154 gave 0·2827 CO_2 and 0·0112 H_2O. C = 66·81; H = 3·96.
$C_{14}H_6O_4(C_2H_3O)_2$ requires C = 66·66; H = 3·70.

It was, therefore, a diacetyl derivative. Thus obtained it forms almost colourless needles, melting at 206°, insoluble in cold dilute alkalis.

The formula and reactions of this substance indicated that it was a hydroxyanthraquinone, and, since it was a dyestuff, that the two hydroxyls it contained were in the ortho-position relatively to one another. It was evidently neither alizarin nor quinizarin, but its properties agreed somewhat closely with those given for *hystazarin*,



Liebermann and Schoeller (*loc. cit.*). Since, however, there appeared to be some slight points of difference between this substance and the one described by these authors, a specimen of hystazarin was prepared from catechol and phthalic anhydride by the method given by them. As a result it was found to be identical with the substance $C_{14}H_8O_4$ in every respect; this fact is of interest, as hystazarin or its compounds have not hitherto been known to exist in plants. In order to determine the methoxy-group evidently present in the substance $C_{15}H_{10}O_4$, it was examined by Zeisel's method.

0·1310 gave 0·1130 AgI. Found CH_3 = 5·50 per cent.
$C_{14}H_7O_3(OCH_3)$ requires CH_3 = 5·90 per cent.

The substance $C_{15}H_{10}O_4$ is therefore *hystazarin monomethyl ether.*

The ammoniacal isobutylic acid mother liquors from which the ammonium salt of hystazarin methyl ether had been deposited, were poured into water, neutralised with acid, and the alcohol boiled off. A lemon-yellow mass was thus obtained, which, after crystallisation from alcohol, was found to consist entirely of the anthragallol dimethyl ether (*B*), melting at 225—227°.

The alcoholic mother liquors (p. 820) obtained during the isolation of the two preceding substances were treated with water, and the small quantity of yellow precipitate thus obtained was collected, washed, and dried. A sample heated with sulphuric acid to 180° yielded no colouring matter, and it was therefore free from the substances described above. By crystallisation from cumene, a yellow glistening mass of fine needles was obtained, which melted at about 270°, but not sharply, and even when further purified the product was not satisfactory in this respect. Analysis gave C = 74.16, H = 3·6 per cent., and since by fusion with alkali, a violet-coloured derivative was obtained, it appeared to be most probably metahydroxyanthraquinone contaminated with a trace of some other substance. What this foreign substance is, it was impossible to say. To determine the point, more of the substance would be required, and to obtain this it would be necessary to work with enormous quantities of raw material. On this account the labour involved would be too great to warrant its investigation.

Extraction by means of Aqueous Sulphurous Acid.

As previously shown, the mixed yellow substances obtained by extraction with sulphurous acid consisted of two anthragallol dimethyl ethers (*A* and *B*), melting at 209° and 225—227° respectively—alizarin α-monomethyl ether, and the so-called resinous substance. The latter could be isolated by the method previously given, but having gained a better knowledge of the characteristic reactions of each constituent, a much more rapid method was now adopted for their separation.

The yellow mass was dissolved in boiling isobutylic alcohol, the hot solution carefully neutralised with ammonia, and the blood-red liquid thus obtained was allowed to stand some hours. The ammonium derivative which crystallised out, contained the whole of the anthragallol dimethyl ether (*A*, m. p. 209°), and the alizarin monomethyl ether, and this was collected, washed with a little of the alcohol, and strongly pressed; it was then treated with acid and the regenerated ethers separated by taking advantage of the well-marked difference of their solubilities in alcohol.

The ammoniacal filtrate, after neutralising with acid, was poured into water and the isobutylic acid boiled off; the yellow liquid, containing a somewhat resinous precipitate in suspension, was then rendered alkaline with ammonia, diluted with half its volume of methylated spirit, and treated with excess of baryta water. On cooling, the barium derivative of the so-called resinous substance separated, and was collected and washed with dilute alcohol. By neutralising the filtrate with acid, a crystalline, yellow precipitate was formed which consisted of almost chemically pure anthragallol dimethyl ether (*B*, m. p. 225—227°).

The barium precipitate suspended in water was neutralised with acid and the product collected, washed, and dried. It was then purified by dissolving it in alcohol, and adding a solution of lead acetate, washing the precipitate with alcohol, and decomposing it with acetic acid. On crystallising it from hot alcohol, the product contained a trace of gelatinous substance, but this was removed by extraction with small quantities of hot methylic alcohol, and the residue was then crystallised from alcohol with the aid of animal charcoal. On analysis it gave the following numbers.

0·1210 gave 0·3003 CO_2 and 0·0443 H_2O. C = 67·68; H = 4·06.
$C_{16}H_{12}O_5$ requires C = 67·60; H = 4·22 per cent.

Thus obtained it consisted of a felted mass of minute orange-yellow needles, melting at 212—213°, and yielding at higher temperatures a sublimate of leaflets. It is readily soluble in alcohol and in acetic acid, sparingly in chloroform; it usually separates from the latter in nodules. Solutions of the alkalis and ammonia dissolve it with a blood-red coloration, but owing to their great solubility, these derivatives were not obtained in a crystalline condition. The barium and lead compounds, as shown above, were useful in the process of purification; the former is obtained as an amorphous red-violet powder, soluble in water, but insoluble in dilute alcohol; the latter as a scarlet precipitate insoluble in cold alcohol and readily decomposed by acetic acid. The red alkaline solutions, when boiled with zinc dust, give the usual reaction of an anthraquinone or allied compound, for they become orange, but regain their original colour on exposure to air.

The acetyl derivative of the substance $C_{16}H_{12}O_5$ was prepared by boiling it with acetic anhydride for three hours, and then adding a little alcohol. On cooling, a crystalline mass was obtained, which, after purification, appeared as orange-coloured leaflets, insoluble in cold alkalis, and melting at 160°. Owing to the small quantity obtained, it could not be analysed, but other results given below show it to be a *monacetyl* derivative. Since there was reason to suspect that the substance $C_{16}H_{12}O_5$ contained a methoxy-group, it was suspended in a little acetic acid and heated in a sealed tube at 180° for one hour with hydrochloric acid. There was thus obtained a glistening mass of red needles, which were collected, washed, dried, and purified by crystallisation from nitrobenzene with the aid of animal charcoal. On analysis, the following numbers were obtained.

0·0518 gave 0·1245 CO_2 and 0·0170 H_2O. C = 65·54; H = 3·64.
$C_{14}H_4O_5$ requires C = 65·62; H = 3·13 per cent.

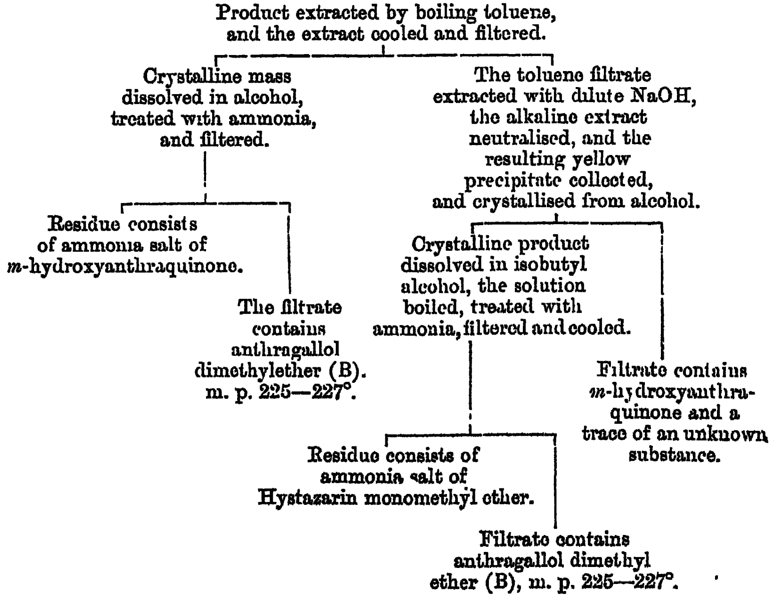
It dissolved in solutions of the alkali hydrates with a green coloration, and had the reactions of anthragallol; its identity with the latter was proved by the melting point of its acetyl derivative, 181—182°. To determine the methoxy-groups contained in the substance, it was examined by Zeisel's method.

0·1071 gave 0·1652 AgI. CH_3 = 9·85 per cent.

$C_{14}H_6O_5(OCH_3)_2$ requires CH_3 = 10·56 per cent.

This shows, therefore, that it is a *dimethyl ether of anthragallol.* It

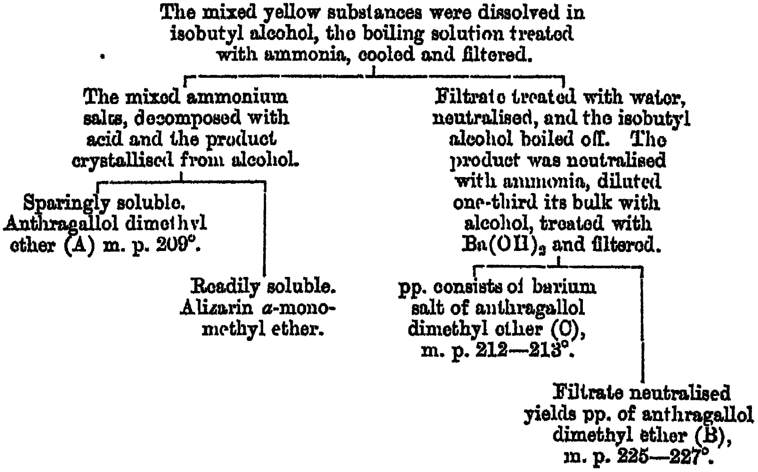
Lime Water Extract of Chay Root.



Product extracted by boiling toluene, and the extract cooled and filtered.

- Crystalline mass dissolved in alcohol, treated with ammonia, and filtered.
  - Residue consists of ammonia salt of *m*-hydroxyanthraquinone.
  - The filtrate contains anthragallol dimethylether (B). m. p. 225—227°.
- The toluene filtrate extracted with dilute NaOH, the alkaline extract neutralised, and the resulting yellow precipitate collected, and crystallised from alcohol.
  - Crystalline product dissolved in isobutyl alcohol, the solution boiled, treated with ammonia, filtered and cooled.
    - Residue consists of ammonia salt of Hystazarin monomethyl ether.
    - Filtrate contains anthragallol dimethyl ether (B), m. p. 225—227°.
  - Filtrate contains *m*-hydroxyanthraquinone and a trace of an unknown substance.

Sulphurous acid Extract.



The mixed yellow substances were dissolved in isobutyl alcohol, the boiling solution treated with ammonia, cooled and filtered.

- The mixed ammonium salts, decomposed with acid and the product crystallised from alcohol.
  - Sparingly soluble. Anthragallol dimethyl ether (A) m. p. 209°.
  - Readily soluble. Alizarin *a*-monomethyl ether.
- Filtrate treated with water, neutralised, and the isobutyl alcohol boiled off. The product was neutralised with ammonia, diluted one-third its bulk with alcohol, treated with $Ba(OH)_2$ and filtered.
  - pp. consists of barium salt of anthragallol dimethyl ether (C), m. p. 212—213°.
  - Filtrate neutralised yields pp. of anthragallol dimethyl ether (B), m. p. 225—227°.

is interesting to find that the three possible substances of this composition exist in chay root. Apart from their melting points and those of their acetyl derivatives, their characteristic distinctions are, that whereas (*A*) and (*C*) form barium derivatives insoluble in dilute alcohol and lead salts, insoluble in cold alcohol, (*A*) alone yields an ammonium derivative, insoluble in cold isobutylic alcohol. The analogous salts of (*B*), on the other hand, are readily soluble in these liquids.

The methods employed for the separation of the yellow substances in chay root, soluble in baryta water, being somewhat intricate, the tables on p. 825 are appended with a view to explain the course pursued more clearly.

Clothworkers' Research Laboratory,
Dyeing Department,
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LXXXV.—*A Modification of Zincke's Reaction.*

By Henry R. Hirst and Julius B. Cohen, Ph.D., Yorkshire College.

In 1889, Cohen and Ormandy showed that aluminium coated with a layer of mercury, prepared by dipping the foil into mercuric chloride solution, formed a couple capable of decomposing water (*Brit. Ass Report*, 1889, 550). This couple was applied to the preparation of pure hydrogen as well as to the estimation of nitrates and nitrites in water analysis (Trans., 1890, **57**, 811). In 1871, Zincke found that if zinc dust is added to a mixture of benzylic chloride and certain aromatic hydrocarbons, and the mixture heated, hydrochloric acid is evolved, and the benzyl group displaces the hydrogen in the nucleus of the aromatic hydrocarbon according to the following equation, taking as an example benzylic chloride and benzene.

$$C_6H_5{\cdot}CH_2Cl + C_6H_6 = C_6H_5{\cdot}CH_2{\cdot}C_6H_5 + HCl.$$

It was found that a similar action occurred if the aluminium couple was employed in place of zinc dust.* As in this case the combination proceeds at the ordinary temperature with only a minute quantity of the couple, we thought that a further study of this obscure action might offer some interest. The product obtained is not, as in Friedel and Craft's reaction, a compound of the hydrocarbon with aluminium chloride, which is subsequently decomposed by water; but in all cases the new hydrocarbon itself is formed, and only small quantities of tarry substances decomposible by water. In this manner, diphenylmethane, phenyltolylmethane, and phenylxylylmethane have been prepared.

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* Radziewanowski (*Ber.*, 1895, **28**, 1135) has shown that a similar reaction is produced by the use of metallic aluminium and gaseous hydrogen chloride or by a mixture of metallic aluminium and solid mercuric chloride.

Diphenylmethane.—Sixty-five c.c. of benzene were placed in a flask attached to a reflux condenser, together with a few pieces of the couple weighing about 0·5 gram. The couple was prepared by shaking up aluminium foil with a saturated solution of mercuric chloride for a minute or two. The liquid was then poured off, the couple washed successively with water, alcohol, ether, and benzene, with as little exposure to the air as possible, and 30 grams of benzylic chloride were slowly added during an hour. On first adding the benzylic chloride, an orange deposit appeared on the bright surface of the foil and gradually covered it; a brisk effervescence, accompanied by considerable rise of temperature, occurred simultaneously, fumes of hydrogen chloride were copiously evolved, and the liquid gradually assumed a brown tint; when all the benzylic chloride had been added, the flask was heated for a short time on the water bath. The liquid, which now consisted of two layers, a tarry mass covering the bottom of the flask and an upper layer of brown, flocculent appearance, consisting mainly of benzene and dissolved hydrocarbon, was shaken up with water containing a little caustic soda, and the benzene separated, the aqueous portion being repeatedly extracted with benzene. The benzene solution was dehydrated over calcium chloride, the benzene distilled off, and the residue fractionated under diminished pressure (80 mm.). The following fractions were obtained.

1.	Below 170°	1·0 gram.
2.	174—176°	14·45 grams.
3.	178—200	2·35 „
4.	Residue	9·3 „

Fraction 2 solidified completely on cooling, and proved to be pure diphenylmethane, m. p. 25—26°.

0·1710 gave 0·5825 CO_2 and 0·11375 of H_2O. C = 92·90; H = 7·38.
$C_{13}H_{12}$ requires C = 92 85; H = 7·14 per cent.

Fractions 3 and 4 were viscid liquids which did not crystallise, and they were not further investigated.

In order to arrive at a more definite idea of the course of the action, the hydrogen chloride which was evolved was estimated by aspirating it through a standard solution of caustic soda. The apparatus consisted of a flask, to which was attached an apparatus for drying the aspirated air, a tap funnel for introducing benzylic chloride gradually, and a reflux condenser, and to the end of the reflux condenser were fitted two vessels containing caustic soda solution. The benzene and the aluminium couple were placed in the flask, and the benzylic chloride diluted with benzene was added in successive portions, air being slowly aspirated through the apparatus all the time. After 3—4 hours, a second piece of aluminium was added, but no further action was apparent, and the flask was then heated on the water bath at intervals, the operation lasting about 24 hours in all.

On removing the flask and pouring off the benzene from the tarry matter, we noticed in one experiment that, after a short exposure to the air, fumes of hydrogen chloride were evolved; this is no doubt due to decomposition of the tarry substance by the moisture in the air, as it is immediately decomposed on the addition of water, yielding a brown oil and hydrochloric acid, which remains dissolved in the water. The following are the results obtained.

I. 19·5 grams of benzene, 10·3 grams of benzylic chloride, and 0·06 gram of aluminium couple gave HCl = 2·52 grams. Theoretical, 2·98.

II. 20 grams of benzene, 10·21 grams of benzylic chloride, and 0·06 gram of aluminium couple gave HCl = 2·61 grams Theoretical, 2·95.

About 86 per cent. therefore of the hydrochloric acid is evolved during the action, the remainder being contained in the portion insoluble in benzene.

Phenyltolylmethane.—The above process was carried out in precisely the same manner with toluene in place of benzene. From 10 grams of benzylic chloride 5·78 grams of an uncrystallisable oil were obtained, boiling at 270—283°. On further fractionation, about one-half boiled at 278—280°, and gave the following results on analysis.

0·1205 gave 0·4080 CO_2 and 0·0857 H_2O. C = 92·4; H = 7·9.
0·1830 „ 0·6118 CO_2 „ 0·1315 H_2O. C = 92·3; H = 7·9.
$C_{14}H_{14}$ requires C = 92·3; H = 7·7 per cent.

About 0·5 gram of a solid substance separated out from the original oil on cooling; when pure, it crystallises in greenish plates with a silvery lustre, and melts at 230—231°. With picric acid in acetic acid solution, a deep crimson coloration is produced, a reaction which is characteristic of anthracene and many of its hydrocarbon derivatives. The quantity was too small to admit of further investigation.

Phenylxylylmethane.—Commercial metaxylene was carefully dehydrated and fractionated, and a portion boiling within 1½° was employed. In this case, a greater variety of products was obtained than in the two previous examples; this may be, in part, due to the fact that the xylene was not chemically pure. The larger portion of the product boiled at 287—296°. The fraction boiling at 289—291° gave on analysis the following results.

0·1600 gave 0·5373 CO_2 and 0·1235 H_2O. C = 91·5; H = 8·5.
0·2444 „ 0 8225 CO_2 „ 0·1900 H_2O. C = 91·7; H = 8·6.
$C_{15}H_{14}$ requires C 91·8; H = 8·2 per cent.

Some experiments by Mr. G. Hefford may be briefly mentioned here, as he is unable to continue them.

The aluminium couple brings about a reaction between chloroform and benzene in presence of gaseous hydrogen chloride with the formation of diphenylmethane and a small quantity of phenylanthracene, melting at 157°, but no triphenylmethane.

Under similar conditions, benzene combines with benzylidene chloride with the formation of diphenylmethane along with other hydrocarbons. The action in these cases is very involved, and a number of products are formed.

LXXXVI.—*A Method for Preparing the Formyl Derivatives of the Aromatic Amines.*

By HENRY R. HIRST and JULIUS B. COHEN, Ph.D., Yorkshire College.

IN studying the constitution of the acid amides, it was thought possible that formamide might react like an aldehyde, combining with phenylhydrazine to form a hydrazone of the formula

$$C_6H_5NH{\cdot}N{:}CH{\cdot}NH_2.$$

On mixing formamide and phenylhydrazine in molecular proportion dissolved in glacial acetic acid and allowing the mixture to remain in the cold, crystals soon began to be deposited, and in a few hours formed a nearly solid mass.

The substance proved to be formylphenylhydrazine,* the action being as follows.

$$C_6H_5{\cdot}NH{\cdot}NH_2 + H{\cdot}CONH_2 + CH_3{\cdot}COOH \doteq C_6H_5{\cdot}NH{\cdot}NH{\cdot}COH + CH_3{\cdot}COO{\cdot}NH_4.$$

As the yield in this case amounted to 82 per cent. of the theoretical, we thought that the reaction, if generally applicable, might furnish an easy method for preparing formyl derivatives of the amines. This has so far proved to be the case with all the primary aromatic amines experimented on, the action taking place in the cold. The secondary aromatic amines containing an alkyl radicle only react on heating, whilst diphenylamine does not combine even on continued boiling. The formyl derivatives of the following bases have been prepared. Aniline, ortho- and para-toluidine, α- and β-naphthylamine, phenylhydrazine, orthotolylhydrazine, methylaniline, ethylaniline, paraphenylenediamine, and benzidine.

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* Compare Just (*Ber.*, 1886, 19, 1201), who prepared this compound by heating phenylhydrazine with formamide at 130°.

The yield in all cases was very satisfactory, so that only a few grams of the base are required for the experiment. The product, after one recrystallisation, was usually quite pure.

Formanilide.—Four grams of aniline and 2 grams of formamide dissolved in 4·8 grams of glacial acetic acid gave 3·2 grams of pure formanilide, m. p. 45—47°.

0·2079 gave 21·4 c.c. moist nitrogen at 14° and 746 mm. N = 11·9.
C_7H_7NO requires N = 11·6 per cent.

Formylorthotoluide, obtained as above, melted at 57—59°.

0·2585 gave 23·4 c.c. moist nitrogen at 12° and 757 mm. N = 10·7.
C_8H_9NO requires N = 10·4 per cent.

Formylparatoluide, after one crystallisation, melted at 50— 53°. It was not analysed.

Formyl-α-naphthalide melted at 137·5°, and gave the following results on analysis.

0·2407 gave 16·6 c.c. moist nitrogen at 12° and 751·5 mm. N = 8·1.
$C_{11}H_9NO$ requires N = 8·2 per cent.

Formyl-β-naphthalide melted at 120—123°.

0·2085 gave 15·4 c.c. moist nitrogen at 16° and 748 mm. N = 8·4.
$C_{11}H_9NO$ requires N = 8·2 per cent.

Formylphenylhydrazide melted at 140°.

0·1610 gave 29·8 c.c. moist nitrogen at 19° and 748 mm. N = 20·6.
$C_7H_8N_2O$ requires N = 20·9 per cent.

Formylorthotolylhydrazide.—This substance, which has not yet been described, crystallises from alcohol in colourless needles, melting at 119°.

0·1910 gave 31·2 c.c. moist nitrogen at 13·5° and 733·5 mm. N = 18·6.
$C_8H_{10}N_2O$ requires N = 18·7 per cent.

Formylmethylanilide.—Three grams of methylaniline, 1·5 gram of formamide, and 3·6 grams of glacial acetic acid were heated for six hours, the liquid poured into water, neutralised with ammonium carbonate, and extracted with ether. 2·7 grams of liquid were obtained, of which the portion boiling at 240—243° (1·1 gram) was analysed.

0·3640 gave 32·6 c.c. moist nitrogen at 14·5° and 749·5 mm. N = 10·36.
C_8H_9NO requires N = 10·4 per cent.

Formylethylanilide.—Three grams of ethylaniline, treated in the same way as methylaniline, gave 2·4 grams of liquid boiling at 240—250°.

0·1983 gave 16 c.c. moist nitrogen at 15° and 751 mm. N = 9·3.
$C_9H_{11}NO$ requires N = 9·3 per cent.

Diformylparaphenylenediamine.—1·3 gram of paraphenylenediamine, 1 gram of formamide, and 2·4 grams of glacial acetic acid were left to stand, and the product crystallised from water. 1·2 gram of a greyish crystalline powder was obtained, melting at 205—207°. The disodium compound of this substance was obtained as a fine white powder by adding a strong solution of caustic soda in alcohol to the alcoholic solution of the formyl compound.

0·1005 gave 0·0665 Na_2SO_4. Na = 21·43.
$C_8H_6N_2O_2Na_2$ requires 22·11 per cent.

Orthophenylenediamine, under similar conditions, appears to form phenyleneformamidine, melting at 168—170°.

Diformylbenzidine, prepared as above, formed a crystalline powder which did not melt at 240°. It was converted into the disodium compound, which was analysed with the following result.

0·0525 gave 0·0278 Na_2SO_4. Na = 16·9.
$C_{17}H_{10}N_2O_2Na_2$ requires Na = 16·19.

LXXXVII.—*The Molecular Refraction of Dissolved Salts and Acids.*

By Dr. JOHN HALL GLADSTONE, F.R.S., and WALTER HIBBERT, F.I.C.

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IN papers on "Refraction Equivalents," published in the *Proc. Roy. Soc.* for 1868, and in the *Phil. Trans.* for 1870, one of us (Gladstone) gave reasons for believing that the law of refraction equivalents holds good in the case of compounds in solution, that is to say, that the refraction equivalent of a solution is the sum of the refraction equivalents of the solvent and of the substance dissolved. If therefore the refraction equivalent, or molecular refraction, of the solvent and its proportionate quantity is known, it is easy to determine the molecular refraction of the salt or other substance in solution. Proceeding on this belief, he determined the molecular refraction of a large number of salts, and deduced from them the atomic refraction of most of the metals. A paper by Janovsky, however, caused some chemists to doubt the correctness of the method, and in 1880 a small committee of the British Association was appointed, "for the purpose of investigating the method of determining the specific refraction of solids from their solutions." The report, drawn up by Professor Phillips Bedson,* detailed various experiments, and arrived at the conclusion that they served to substantiate the law given above.

Professor Kanonnikoff, of Kazan, in 1883, being unaware of what had previously been done, adopted the same method, and, as far as his experiments went, arrived at similar results.

Other researches on dissolved substances brought forth an accumulation of evidence in favour of this law, but, at the same time, it became more and more probable that in certain cases the law was only approximately true. It appeared desirable, therefore to us that the question should be more carefully investigated, especially as the apparent exceptions to a general law are often very fruitful of fresh discovery. We now submit to the Society the results of our own recent experiments, together with those of other observers in the same field.

In the paper in the *Phil. Trans.* already referred to, five reasons are given for confidence in the law. They are essentially as follows.

1. The similarity of the refraction equivalents of certain substances when determined for the solid and from its solution.

2. The close agreement of the refraction equivalent of several organic compounds when dissolved in water with what might be

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* All references will be given in Appendix II.

calculated from the values for carbon, hydrogen, and oxygen, as determined by Landolt.

3. That the refraction equivalent, as reckoned from a solution, is not affected by varying the amount of water.

4. The similarity of the refraction equivalent of the salt, whether water or alcohol be the solvent.

5. The constancy of the differences of refraction presented by corresponding series of salts in solution.

We propose in this paper to deal only with Nos. 1 and 3, and that in reference only to salts and acids.

Historical Development.

The instance specially cited in the original paper of 1870, in support of the view that the molecular refraction was constant, was that of sodium chloride. There was a series of observations on solutions of this salt in water, varying in strength from 23·2 to 8·7 per cent. The molecular refraction for the line A varied irregularly about the mean figure 15·42, the extremes being 15·26 on one side, and 15·55 on the other. The same constancy was claimed for other salts, and an examination of the data would seem to warrant the claim in regard to several, but none of these were examined in weak solution, nor indeed through any wide range of strength.

There had been previously published several tables of the refractive indices and densities of solutions of the same salt at different degrees of concentration. From these data, we have calculated the molecular refraction, and the results are given in Appendix I (p. 864, *et seq.*). Thus calculated, Kremer and Beer's tables, published in 1857, indicate for many salts little or no change on dilution.

The figures of Handl and Weiss in 1858, of Landolt in 1862, of Wüllner in 1869, and of Damien in 1881, lead to a similar conclusion. Only those of Schmidt, in 1859, seem to indicate a totally different result.

Subsequent to 1870, Van der Willigen published some elaborate investigations showing little variation, and E. Forster, in 1878, concluded that the specific refractive energy of salt solutions is not so constant as with mixtures of liquids, but that the variations are generally within 1 per cent. of the mean. In Appendix I, the observations of Wüllner, Van der Willigen, and Damien have been reduced by means of their own values for water, in other cases we have used our own.

A second paper by one of the authors (Gladstone), which appears in the *Transactions of the Chemical Society* for 1891, establishes the fact that the value for hydrochloric acid does change with a varying amount of water, that this change is considerable, and that with an increasing percentage of substance in the solution the refraction becomes smaller. It shows that the same is true of molecular dispersion, the change here being proportionately greater. The same holds good also, though not to the same extent, with other acids, whilst in the case of salts, the evidence is rather in favour of constancy. About the same time, Le Blanc, Wegner, Schütt, and more recently De Muynck, have made determinations on certain groups of acids and salts.

There are other observations, principally by foreign physicists, which would be valuable in this connection, if they had given the density of the solution.

This was the condition of the question when we took it up for re-examination. Since that time, Hallwachs and Kohlrausch, using refined methods for determining the refractive index and the density, have carried the investigation into the region of the most dilute solutions. We have reason also to believe that Nasini has been bringing his great powers of investigation to bear on the same general question.

The Data.

The data employed in this investigation include:

1. Gladstone's old observations (1868—1891) whenever they were considered sufficiently trustworthy and valuable for our present purpose. They have generally been recalculated by means of the value for water which we now employ.

2. The published observations of others. All those mentioned in the introduction are included, unless there was some obvious ground for their omission, and they are calculated out to the molecular refraction.

These two constitute Appendix I.

3. The published observations on such solids and anhydrous liquids as have also been examined in solution.

4. Our own most recent observations; these were usually made in much the same way as that previously described. But as it was no part of our special object to measure the dispersion; as the hydrogen and sodium lines can be made use of at any time; and as most of our Continental fellow-workers have made use of these lines in the spectrum, we have also employed them.

Seeing that the molecular refraction of the salt is the difference between the molecular refraction of the solution and that of the water, it is evident that all experimental errors, as well as all errors arising from impurity of substance, must be accumulated on the very thing we are seeking—the refraction due to the salt itself. We have therefore determined with great care the molecular refraction of the water employed for the different series of experiments. The figures we have generally found are the following.

Water at 18° C.

	H_{α}.	D.	H_{β}.
μ	1·3315	1·3334	1·3375
$(\mu - 1)/d$	0·3318	0·3337	0·3378

It is evident also that the chance of error is greatly increased if the amount of salt is only a small fraction of the solution; so that with all precautions we do not feel justified in placing much reliance on the figures yielded by solutions weaker than 5 per cent., although in a few cases we have placed on record figures obtained from solutions still more dilute.

Table I contains the name of the substance, its formula, the percentage of the substance in the solution, and the molecular refraction for the hydrogen line α or C, the sodium line D, and the hydrogen line β or F.

TABLE I.

Substance.	Formula.	Percentage.	R_{α}.	R_{D}.	R_{β}.
Hydrochloric acid	HCl	38·93	14·02	14·14	14·46
” ”	”	34·30	14·11	14·23	14·55
” ”	”	23·00	14·25	14·37	14·72
” ”	”	13·18	14·33	14·45	14·80
” ”	”	5·23	14·50	14·58	14·94
” ” 2nd spec.	”	30·10	—	14·29	
” ” ”	”	25·70	—	14·31	
” ” ”	”	20·96	—	14·38	
” ” ”	”	13·63	—	14·43	
” ” ”	”	6·87	—	14·50	
” ” ”	”	3·47	—	14·96	
” ” 3rd spec.	”	21·10	14·48	—	14·93
” ” ”	”	7·60	14·57	—	15·08
Lithium chloride.........	LiCl..........	43·40	—	14·47	
” ”	”	24·10	—	14·80	
” ”	”	13·10	—	14·82	
” ”	”	10·59	—	15·02	
” ”	”	6·77	—	14·89	
” ”	”	5·10	—	15·07	
” ” 2nd spec.	”	48·50	14·23	—	14·64
” ” ”	”	39·80	14·44	—	14·83
” ” ”	”	39·52	14·46	—	14·87
” ” ”	”	25·90	14·65	—	15·06
” ” ”	”	19·09	14·75	—	15·22
” ” ”	”	12·74	14·89	—	15·26
” ” ”	”	6·93	14·99	—	15·38
Sodium chloride	NaCl	25·80	—	15·80	
” ”	”	4·61	—	15·94	
” ” 2nd spec.	”	26·41	15·68	—	16·11
” ” ”	”	8·32	15·84	—	16·20

TABLE I (*continued*).

Substance.	Formula.	Per-centage.	R_a.	R_D.	R_β.
Potassium chloride	KCl	23·00	18·16	18·58	18·90
„ „	„	12·40	18·46	18·62	18·98
„ „	„	6·16	18·44	18·48	18·97
Rubidium chloride	RbCl	28·81	—	22·26	
„ „	„	15·07	—	22·30	
„ „	„	9·20	—	22·04	
„ „	„	3·94	—	22·30	
Ammonium chloride	NH_4Cl	25·64	22·35	22·47	22·84
„ „	„	25·21	22·35	22·48	22·88
„ „	„	6·20	22·41	22·50	22·85
„ „	„	5·57	22·70	22·51	23·10
Magnesium chloride	$MgCl_2$	33·92	—	29·02	
„ „	„	13·52	—	29·20	
„ „	„	6·89	—	29·24	
Calcium chloride	$CaCl_2$	39·55	—	32·35	
„ „	„	17·83	—	32·69	
„ „	„	9·57	—	32·93	
„ „	„	4·96	—	32·93	
Strontium chloride	$SrCl_2$	32·06	—	35·02	
„ „	„	18·44	—	35·23	
„ „	„	9·71	—	35·29	
Barium chloride	$BaCl_2$	24·64	—	38·91	
„ „	„	12·36	—	39·21	
„ „	„	6·38	—	39·24	
Cobalt chloride	$CoCl_2$	27·86	32·71	32·97	
„ „	„	17·49	32·84	33·12	
„ „	„	9·47	32·77	32·99	
„ „	„	4·97	32·86	33·53	
Copper chloride	$CuCl_2$	36·59	—	33·73	
„ „	„	6·85	—	33·18	
„ „ 2nd spec.	„	42·45	—	33·82	34·99
„ „ „	„	39·20	—	33·66	34·84
„ „ „	„	23·30	—	33·60	34·55
„ „ „	„	11·60	33·17	33·32	34·50
„ „ „	„	6·08	32·76	33·00	34·44
Ferric chloride	$FeCl_3$	40·66	—	53·95	
„ „	„	5·19	—	52·31	
„ „ 2nd spec.	„	44·80	53·32	54·63	
„ „ „	„	41·30	53·07	51·32	
„ „ „	„	35·11	52·70	53·17	
„ „ „	„	20·50	52·08	52·94	
„ „ „	„	10·95	51·84	52·65	
„ „ „	„	5·72	51·68	52·55	
Gold chloride	$AuCl_3$	61·70	59·27	60·35	
„ „	„	7·57	56·97	58·50	
Platinum chloride	$PtCl_4$	39·40	78·22	79·81	
„ „	„	21·68	77·57	79·03	
„ „	„	8·10	77·20	78·39	
Gold sodium chloride	$AuCl_3,NaCl$	52·90	74·33	75·63	
„ „	„	33·10	74·36	75·70	
„ „	„	11·63	74·90	75·99	79·43
„ „	„	6·10	74·29	75·77	79·57
Hydrobromic acid	HBr	44·82	—	20·61	
„ „	„	26·60	—	20·78	

TABLE I (*continued*).

Substance.	Formula.	Percentage.	R_α.	R_D.	R_β.
Hydrobromic acid	HBr	14·72	—	20·89	
" "	"	7·74	—	21·04	
" "	"	3·84	—	21·10	
Potassium bromide	KBr	38·20	—	25·38	
" "	"	8·49	—	25·46	
Gold bromide	$AuBr_3$	11·69	82·32		
" "	"	6·14	83·62		
Hydriodic acid	HI	65·30	—	32·15	
" "	"	22·96	—	32·34	
" "	"	12·50	—	32·38	
" "	"	6·56	—	32·48	
" " 2nd spec.	"	55·55	31·68	32·13	
" " "	"	43·64	31·85	32·04	
" " "	"	26·00	31·63	32·20	
" " "	"	14·36	31·88	32·35	
" " "	"	7·57	31·75	32·35	
Potassium iodide	KI	43·67	—	36·62	
" "	"	7·25	—	36·55	
" "	"	3·74	—	36·19	
" " 2nd spec.	"	57·17	36·02	36·52	37·74
" " "	"	35·84	36·07	36·51	37·70
Ammonium iodide	NH_4I	53·80	—	40·22	
" "	"	8 92	—	40·29	
" "	"	59·50	39·69	40·22	41·63
" "	"	33·95	39·35	40·09	41·53
" "	"	18·86	39·27	39·90	41·27
" "	"	10·00	38·93	39·74	41·09
Nitric acid	HNO_3	88·00	16·27	16·37	16·67
" "	"	53·60	16·80	17·01	17·36
" "	"	21·37	17·34	17·49	17·94
" "	"	17·80	17·27	17·41	17·83
" "	"	6·30	17·27	17·41	17·91
" " 2nd spec.	"	40·98	17·08	17·24	17·65
" " "	"	32·08	17·17	17·33	17·76
" " "	"	24·35	17·39	17·51	17·95
" " "	"	6·00	17·32	17·51	17·97
Lithium nitrate	$LiNO_3$	42·18	17·73	17·91	18·29
" "	"	39·77	17·79	17·91	18·31
" "	"	23·50	17·87	17·99	18·40
" "	"	10·50	17·73	17·81	18·24
" "	"	5·12	17·76	17·72	18·23
" " 2nd spec.	"	60·40	17·77	17·91	18·29
" " "	"	52·40	17·95	18 07	18·47
" " "	"	27·53	17·76	17·93	18·43
" " "	"	14·90	17·72	17·86	18·31
" " "	"	7·77	17·52	17·61	17·95
Potassium nitrate	KNO_3	17·55	—	22·26	
" "	"	9·24	—	22·29	
" "	"	4·76	—	22·24	
Silver nitrate	$AgNO_3$	44·51	—	27·11	
" "	"	5·88	—	26·60	
" " 2nd spec.	"	62·30	27·113	27·36	28·04
" " "	"	31·21	26·87	27·07	27·75
" " "	"	14·80	26·64	26·89	27·55
" " "	"	7·90	26·38	26·44	27·45

TABLE I (*continued*).

Substance.	Formula.	Percentage.	R_{α}.	R_D.	R_{β}.
Barium nitrate	$Ba(NO_3)_2$	9·87	44·53	44·78	45·72
" "	"	6·77	44·55	44·61	45·33
" "	"	4·24	44·45	44·68	45·67
Lead nitrate	$Pb(NO_3)_2$	35·94	—	54·12	
" "	"	7·04	—	53·32	
" " 2nd spec.	"	34·60	53·14	53·67	55·24
" " "	"	20·23	52·88	53·50	54·93
" " "	"	11·07	52·17	53·12	54·35
Sulphuric acid	H_2SO_4	23·00	22·94	23·06	23·36
" "	"	15·98	22·82	22·97	23·22
" "	"	10·10	22·79	22·84	23·15
" "	"	5·25	22·74	22·76	23·28
" "	"	3·25	23·16	23·10	23·64
" " 2nd spec.	"	97·50	22·34	22·44	22·68
" " "	"	85·25	22·42	22·54	22·80
" " "	"	83·00	22·53	22·65	22·92
" " "	"	37·20	22·73	22·88	23·20
" " "	"	21·00	22·86	22·96	23·07
" " "	"	11·30	22·96	22·94	23·22
" " "	"	5·80	23·00	22·75	22·92
" " 3rd spec.	"	98·00	22·32	22·47	22·66
" " "	"	89·75	22·44	22·55	22·80
" " "	"	84·70	22·46	22·59	22·88
" " "	"	81·80	22·48	22·62	22·91
" " "	"	80·05	22·49	22·61	22·87
" " "	"	77·25	22·49	22·60	22·85
" " "	"	71·90	22·56	22·66	22·92
" " "	"	63·20	22·51	22 65	22·94
Sodium sulphate	Na_2SO_4	30·40	26·54	26·63	26·99
" "	"	10·93	26·16	25·93	26·30
" "	"	5·75	26·54	25·84	26·04
Potassium sulphate	K_2SO_4	10·44	—	32·41	
" "	"	5·43	—	32·55	
Rubidium sulphate	Rb_2SO_4	30·84	38·39	38·58	39·06
" "	"	17·53	38·42	38·58	38·98
" "	"	9·42	38·53	38·17	39·22
Cæsium sulphate	Cs_2SO_4	58·26	47·53	47·78	48·36
" "	"	27·08	47·42	17·93	48·51
" "	"	15·24	46·99	47·60	48·47
Magnesium sulphate	$MgSO_4$	25·76	24 00	—	24·32
" "	"	18·20	24·10	—	24·36
" "	"	11·47	24·19	—	24·43
Zinc sulphate	$ZnSO_4$	32·50	—	26·32	
" "	"	8·30	—	27·02	
Potassium zinc sulphate	$K_2SO_4,ZnSO_4,6H_2O$	11·94	95·77	95·91	98·08
" " "	"	8·41	95·95	96·03	98·01
Ammonium zinc sulphate	$(NH_4)_2SO_4,ZnSO_4,6H_2O$	11·86	102·47	103·10	104·23
" " "	"	6·13	102·26	103·46	105·60
Sodium chlorate	$NaClO_3$	47·10	21·79	22·00	22·15
" "	"	27·60	22·33	21·95	22·38
" "	"	6·58	22·11	21·87	22·42

ADDENDA.

Substance.	Formula.	Percentage	R_A.	R_F.	R_H.
Lithium chloride	LiCl..........	39·52	14·51	15·04	15·49
" "	"	25·87	14·89	15·43	15·96
" "	"	14·53	15·09	15·70	16·20
" "	"	10·03	15 45	16 00	16 50
Hydrobromic acid	HBr..........	44·50	20 07	—	22·19
" "	"	7·80	20 64	—	22·43

Solids and their Saturated Solutions.

As a salt in the solid condition is presumably a more simple body than when it is dissolved in water, and after it may have suffered dissociation or combination with the solvent or its elements, it is most logical to commence by considering whether any change in specific refraction is effected by the act of solution.

Unfortunately there exist very few observations of the refraction of solid salts which are available for our purpose. Nearly all crystallised salts have more than one index of refraction. Again, few observers have given the sp. gr. of the actual specimen of salt from which they have determined its optical properties. Nevertheless we have been able to find determinations of 14 solid substances of simple refraction which answer our purpose, and of 8 other salts which have more than one index of refraction, but so near together that the mean of the two or three indices may be considered as very close to the refraction which the substance would exhibit if it had only one index.

The following table gives these substances in the first column, then the spectrum line observed, after that the molecular refraction of the substance, first as a solid and then in a saturated or nearly saturated solution. The next two columns show the actual difference of the two values and the percentage change respectively, the + sign meaning an increase on solution, the — sign a decrease. In the case of more than one index of refraction, the mean is taken. The final columns give the initials of the observers. Appendix II (p. 867) will explain these and give references.

The list commences with Sir Isaac Newton, whose work included the density as well as the refraction of substances. It will be seen that in drawing up this table, we are greatly indebted to the work of Messrs. Topsoe and Christiansen on crystals. We have also to thank Mons. L. Perrot and Mr. Tutton for supplying us with specimens for solution.

TABLE II.

Salt.	Line.	Molecular refraction.		Change on solution.		Observers.	
		Solid.	Solution.	Actual.	Percentage.	Solid.	Solution.
Sodium chloride	Red	14·88	15·68	+0·8	+5·37	N	H
„	A	14·75	15·56	+0·81	+5·46	Bl	v d W.
„	„	14·56	15·4	+0·84	+5·77	G	G
„	α	14·63	15·7	+1·07	+7·31	Bd	Bd
„	D	14·78	15·80	+1·02	+6·97	Gr	H
„	„	14·78	15·76	+0·98	+6·63	Hg	Hl
Potassium chloride	„	18·72	18·58	−0·14	−0·52	Rub	H
Ammonium chloride	α	22·35	22·35	0·0	0·0	Gr	„
Potassium bromide	D	24·85	25·38	+0·53	+2·1	T & C	„
Potassium iodide	α	35·84	36·0	+0·16	+0·44	„	D
„	D	36·29	36·52	+0·23	+0·63	„	H
Ammonium iodide	„	40·81	40·22	−0·59	−1·44	„	„
Sodium chlorate	F	22·52	22·15	−0·37	−1·65	Dus	„
Sodium alum	D	241·0	241·2	+0·2	+0·08	S	G
Ammonium alum	„	255·2	256·8	+1·6	+0·63	S	„
Barium nitrate	„	45·8	44·78	−1·02	−2·22	T & C	H
Lead nitrate	„	57·26	54·12	−3·14	−5·49	„	„
Sodium metaphosphate	A*	19·0	19·48	+0·48	+2·53	Bd	Bd
Borax (fused)	A*	42·80	42·83	+0·03	+0·07	„	„
Boric acid	α	15·20	14·77	−0·43	−2·8	„	„
Two indices.							
Silver nitrate	D	28·45 30·76	27·11	−2·47	−8·4	Br	H
Three indices.							
Potassium sulphate	α	32·22 32·14 32·39	32·15	−0·1	−0·31	Tut	K
„	D	32·45 32·77 32·54	32·41	+0·18	+0·55	T & C	H
Rubidium sulphate	α	37·83 37·74 37·75	38·39	+0·62	+1·6	Tut	„
Cæsium sulphate	„	48·05 47·89 47·50	47·57	−0·24	−0·5	„	„
Magnesium sulphate	„	62·54 66·46 65·78	65·87	+0·94	+1·4	T & C	„
Zinc sulphate	„	65·00 68·82 68·30	68·8	+1·43	+2·1	„	K
„	D	65·32 69·16 68·66	69·1	+1·39	+2·04	„	G
Potassium zinc sulphate	„	94·06 95·27 97·84	95·94	+0·22	+0·23	Perr	H
Ammonium zinc sulphate	„	101·22 102·14 103·41	103·47	+1·21	+1·19	„	„

* This is the A of Cauchy's formula.

From the above table we may at once draw the following conclusions.

1. That in every instance the molecular refraction of the salt is not very different in the solid and dissolved conditions.

2. That in the majority of cases there is a difference which can scarcely be attributed to errors of observation. The greatest difference occurs in the case of sodium chloride, and of lead and silver nitrate, whilst in the case of the alums, potassium iodide, and perhaps one or two other substances, the difference is so small that it may be purely accidental.

3. That the change of refraction of a salt when dissolved is sometimes in the direction of increase, and at other times in the direction of decrease. Thus nearly all the haloïd salts of the metals give an increase on solution; whilst the three nitrates show the opposite effect.

4. As to the salts which exhibit three indices of refraction, the data are scarcely sufficient to allow of our drawing any deductions beyond the general one, that there is no great departure from the mean of these indices when the crystals are dissolved.

5. Six of the salts examined contain water of crystallisation. As they give nearly the same molecular refraction in the solid and dissolved condition, it is evident that there can be little or no difference produced by the liquefaction of the water of crystallisation.

Other deductions from this table must be reserved till after we have considered the effect of diluting the saturated solutions.

Anhydrous Liquids and their Solutions.

Besides the solids, we have eight substances of which the refraction is known when they are in a liquid condition. They are all acids. There are the three halogen acids, HCl, HBr, and HI, all of which exist as a gas at ordinary temperatures; but they can be liquefied by pressure and cold, and the refraction of the liquids so produced has been determined by Bleekrode. There is HCN, which is a liquid at ordinary temperatures; and there are nitric, sulphuric, formic, acetic, and propionic acids; these last five are miscible with water in all proportions.

The following table is on the lines of Table II, with the addition of another column for the gas in the case of the halogen acids. It must also be explained that whereas the refraction equivalent for the solution in the case of the first three entries represents the effect of the minimum amount of water required to convert the anhydrous acid into a solution, in the subsequent cases, where the acid is perfectly miscible with water, the point of comparison is taken more arbitrarily.

TABLE III.

Substance.	Line.	Liquid.	Gas.	Solution.	Actual change.	Observer.		
		R.	R.	R.		Liquid.	Gas.	Solution
Hydrochloric acid ...	D	10·98	9·959	14·14	+4·16	Blk	Mas	H
Hydrobromic acid....	,,	16·15	12·745	20·77	+4·62	,,	,,	G
Hydriodic acid.......	,,	26·28	20·25	32·15	+5·87	,,	,,	H
Hydrocyanic acid	,,	10·19	9·732	9 85	−0·34	B & B	,,	B & B
Nitric acid	A	16·22*	—	16·39	+0·17	G	—	G
Sulphuric acid	α	22·34†	—	22·53	+0·19	H	—	H
Formic acid	,,	13·91	—	14·07	+0·16	Lan	—	Lan
Acetic acid	,,	21·13	—	21·30	+0·17	,,	—	,,
Propionic acid	,,	28·62	—	28·79	+0·17	,,	—	,,

* 98·7 per cent. † 97·5 per cent.

A glance at this table is sufficient to show that, in the case of hydrogen chloride, hydrogen bromide, and hydrogen iodide, we have a very great increase on solution, far greater, in fact, than in any of the cases where solids were dissolved; it amounts to some 26 per cent. if we compare it with the liquid, and very much more if compared with the gas. On the other hand, in the case of hydrogen cyanide, nitric acid, and sulphuric acid, and especially in the case of the three organic acids, we have no sudden transition from the liquid to the dissolved condition.

Varying Strengths of Solution.

We now come to consider the effect of increasing the amount of water in which the salt or acid is dissolved. For this we have the very large amount of evidence contained in Appendix I and Table I. To bring this into one general view, we have drawn up the following table. The whole evidence cannot be tabulated, so we have included only that derived from the weakest and strongest solutions of the same salt, and for this purpose few solutions of less than 5 per cent. have been admitted, for reasons already explained, except in the case of Kohlrausch and Hallwach's determinations.

As the comparison on which we are now entering deals with figures whose variations are always near to the limits of experimental error, we think it well to indicate what we believe to be the accuracy of our more recent figures. The index may be considered correct to one in the fourth decimal place, so taking $\mu = 1·4000$, the error in the determination of $\mu - 1$, may be somewhere about 1 in 4000. The density was generally determined with a possible error of 1 in 8000, or including a possible want of coincidence between the temperatures at which the index and the density were determined, 1 in 6000. Errors in the determination of the strength of solution will depend very much on the nature of the salt itself and the methods of its analysis; but we consider that it is usually not more than 0·1 per cent. This is unimportant where the specific refraction of the salt is very nearly the same as that of water, but tells where the specific refraction varies greatly in either direction. The value taken for water also affects the result most when the specific refraction is very different. It must be remembered, too, that these different sources of error may either be added together, or may tend to neutralise one another, in any given observation. The aggregate error, of course, falls entirely upon the determination of the salt itself, and when that constitutes only 5 per cent. of the solution, it may be taken at possibly somewhat less than 1 in 100 in the more recent work marked H. In strong solutions, the total error is, of course, less. But in many cases this possible error is diminished by our having taken more than one series of observations on the same substance, and often with different apparatus.

The table is constructed in the following manner. Column 1 contains the name of the substance. Column 2, the formula. Column 3, the line of the spectrum observed. Column 4 gives the highest and lowest percentages of salt or acid, p_1 and p_2, contained in the solutions that have been employed. Column 5 gives the corresponding molecular refractions R_1 and R_2. Column 6 gives the average change in molecular refraction for 1 per cent. change in strength of solution, $\frac{R_2 - R_1}{p_1 - p_2}$. The signs + or − indicate whether the change on dilution is in the direction of increase or decrease respectively. It was thought undesirable to extend these figures beyond the third decimal place, and when the number is less than 0·005, and thus clearly within the limits of experimental error, we have not entered it, but simply indicated the tendency. In judging also of their value, it must be remembered that no account is taken of any intermediate observations; and that the range of strength employed by different observers, or by the same observer at different times, often varies greatly. This is especially the case with the observations of Kohlrausch and Hallwachs on very weak solutions. These really show scarcely any change, but on account of the short percentage-range in strength, appear to show more change than stronger solutions do. We have therefore put the sign only. The last column gives the initials of the observer.

TABLE IV.

Substance.	Formula.	Line.	Change in strength, p_1 to p_2.	Change in molecular refraction, R_1 to R_2.	Average rate of change, $\frac{R_2 - R_1}{p_1 - p_2}$	Observer.
Hydrochloric acid	HCl	F	36·09— 5·13	14·54—15·12	+0·019	G
,, ,,	,,	,,	21·1 7·6	14·93—15·08	+0 011	H
,, ,,	,,	D	30·1 — 6·87	14·29—14·55	+0·011	,,
,, ,,	,,	,,	38·93 5·23	14·14—14·58	+0·013	,,
,, ,,	,,	,,	1·20— 0·025	14·44—14·57	+	Kl & Hl
,, ,,	,,	,,	24·36— 7·45	13·95—14·47	−0·03	Le Bl
Lithium chloride	LiCl	Red	40·0 —24·5	14·42—14·76	+0·022	Kr & Br
,, ,,	,,	C	48·5 — 6·93	14·23—14·99	+0·018	H
,, ,,	,,	D	43·4 — 5·1	14·47—15·07	+0·016	,,
,, ,,	,,	α	11·72— 5·84	14·83—14·82	−	Weg
Sodium chloride	NaCl	A	23·2 — 8 7	15·33—15·30	−	G
,, ,,	,,	,,	26·58— 8·65	15·56—15·47	−0·005	v.d.W.
,, ,,	,,	C	26·41— 8·32	15·68—15·84	+0·0088	H
,, ,,	,,	D	25·80— 4·61	15·80—15·94	+0·0066	,,
,, ,,	,,	,,	14·0 — 0·72	15·76—15·84	+0·006	Kl & Hl
,, ,,	,,	,,	1·44— 0·03	15·79—15·79	0	,,
,, ,,	,,	α	25·0 — 1·0	15·70—15·82	+0·005	Sch
,, ,,	,,	D	24 13— 4·79	15·72—15 80	+	Le Bl
,, ,,	,,	α	24 73— 7·99	15·70—15·76	+	Weg
Potassium chloride	KCl	A	24·1 —12·1	18·70—18·60	−0·008	G
,, ,,	,,	D	23·0 — 6·16	18·58—18·18	−0·006	H
,, ,,	,,	α	9·92— 4 99	18·97—18·95	−	Weg
Rubidium ,,	RbCl	D	28·81 3 94	22·26—22·30	+0·0016	H
Ammonium chloride	NH_4Cl	A	24·83—11·79	22·19—22·14	−	v.d.W.
,, ,,	,,	α	25·64— 5·57	22·35—22·70	+0·017	H
Magnesium ,,	$MgCl_2$	D	33·92— 6·89	29·02—29·24	+0·008	,,
Calcium chloride	$CaCl_2$	Red	40·4 —24·75	31·51—32·01	+0·032	Kr & Br
,, ,,	,,	A	40·64—16·75	31·89 —32·06	+0 007	v.d.W.
,, ,,	,,	D	39 55— 4·96	32·35—32·93	+0·017	H
Strontium chloride	$SrCl_2$	Red	32·00—19 93	34·49—34·46	+0·0025	Kr & Br
,, ,,	,,	D	32·06— 9·71	35·02—35·29	+0·012	H
Barium chloride	$BaCl_2$	,,	24·64 — 6·38	38·91—39·21	+0·017	,,
Cobalt ,,	$CoCl_2$	α	29·86 — 4·07	32·71—32·86	+0·006	,,
Copper ,,	$CuCl_2$	D	36·59— 6·85	33·73—33·18	−0·018	,,
,, ,,	,,	,,	42·15— 6·08	33·82—33·00	−0·022	,,
Zinc chloride	$ZnCl_2$	α	71·8 —35·9	31·32—31·36	+0·007	Will
,, ,,	,,	A	38·98—23 0	30·59—31·03	+0·028	v.d.W.
,, ,,	,,	,,	46·1 —35·3	30·52—30·63	+0·010	G
Cadmium chloride	$CdCl_2$	,,	57·52—14·76	36·09—36·14	+	de M
Ferric chloride	$FeCl_3$	α	40·66— 5·19	53·95—52·31	−0·049	H
,, ,,	,,	α	44·80— 5·72	53·32—51·68	−0·042	,,
Gold chloride	$AuCl_3$	D	61·7 — 7·57	60·35—58·5	−0·034	,,
Platinum chloride	$PtCl_4$	,,	39·4 — 8·1	79·81—78·39	−0·045	,,
Gold sodium chloride	$AuCl_3,NaCl$	,,	52·9 — 6·1	75·63 75·77	+	,,
Hydrobromic acid	HBr	F	65·59—15·47	20·80—21·83	+0·020	G
,, ,,	,,	D	44·82— 7·74	20·61—21·04	+0·012	H
,, ,,	,,	A	44·5 7·85	20·10—20·64	+0 0146	G
Lithium bromide	LiBr	α	9·28— 4·02	21 05—20·9	−0·03	Weg
Sodium ,,	NaBr	Red	45·2 —28·87	22·09—22·27	+0·011	Kr & Br
,, ,,	,,	α	31·02— 4·95	21·83—21·89	+	Weg
Potassium bromide	KBr	,,	37·7 —23·2	25·6 —25·53	−0·005	Kr & Br

TABLE IV (*continued*).

Substance.	Formula.	Line.	Change in strength, p_1 to p_2.	Change in molecular refraction, R_1 to R_2.	Average rate of change, $\dfrac{R_2 - R_1}{p_1 - p_2}$	Observer.
Potassium bromide ..	KBr.......	D	38·2 — 8·49	25·38—25·16	+	H
„ „ ..	„	*a*	19·82— 5·01	25·17—25·21	+	Weg
Calcium bromide....	$CaBr_2$	Red	55·9 —38·9	44·01—44·78	+0·015	Kr & Br
Strontium bromide ..	$SrBr_2$......	„	48·56—32·2	47 29—47·21	−0·005	„
Barium bromide	$BaBr_2$	„	50·50—33·60	53 07—53·04	−	„
Cadmium bromide...	$CdBr_2$	D	33·29 —11·98	49·37—49·75	+0·018	de M
Gold bromide.......	$AuBr_3$.....	*a*	11·69— 6·14	82·32 83·62	+0·240	H
Hydriodic acid......	HI........	D	65·3 — 6·56	32·15 —32·18	+0·006	„
„ „	„	„	55·55— 7·57	32·13—32·35	+0·005	„
Lithium iodide	LiI........	*a*	10·54— 3·08	31·90 - 31·88	−	Weg
Potassium iodide.. .	KI........	Red	55·05- 37·90	36·26 36·18	+0·013	Kr & Br
„ „	„	*a*	55·12 -18·70	36·06 -35·61	−0·010	Dam
„ „ ..	„	D	13·67— 7·25	36·62—36·55	−	H
„ „	„	„	57·17—35·84	36·52—36·54	+	„
„ „	„	*a*	20·04— 5·01	36·17—36·29	+0·008	Weg
Ammonium „	NH_4I......	D	53·81— 8·92	40·22—10·29	+	H
„ „	„	„	59·5 —10·0	40·22—39·74	−0·01	„
Cadmium iodide	CdI_2.......	„	31·12— 9·56	72·03—70·47	−0·07	de M
Sodium iodide	NaI	*a*	14·70— 6·25	32·85—32·93	+0·01	Weg
Sulphuric acid......	H_2SO_4.....	C	94·3 —17·05	22·97—23·80	+0·011	Hd & W
„ „	„	„	94·72—23·29	22·36—22·52	+	v.d.W.
„ „	„	*a*	23·0 — 5·25	22·94—22·74	−0·011	H
„ „	„	„	97·5 — 5·8	22·34—23·0	+0·007	„
„ „	„	„	98·0 —63·2	22·32—22·51	+0·005	„
„ „	„	D	94·11— 4·78	22·23—22·82	+0·006	Le Bl
„ „	„	„	2·35— 0·050	22·9 —23·2	+	Kl & H
Sodium sulphate	Na_2SO_4....	A	10·51— 6·8	26·20—26·14	−0·016	v.d.W.
„ „	„	„	14·10 - 7·19	24·32 - 23·88	−0·064	F
„ „	„	*a*	30·4 — 5·75	26·54—25·54	−0·040	H
„ „	„	D	25·51— 4 76	26·30—26·23	−	Le Bl
Potassium sulphate..	K_2SO_4.....	„	10·41— 5·43	32·41—32·55	+0·024	H
Magnesium „ ..	$MgSO_4$	*a*	25·76—11·17	24·00—24·19	+0·013	„
„ „ ..	„	D	1·47 - 0·03	24·14—24·26	+	Kl & H
Zinc sulphate	$ZnSO_4$	„	32·5 — 8·3	26·32 27·02	+0·020	H
„ „	„	„	1·58— 0·033	27·10—27·08	−	Kl & H
Sodium chlorate.....	$NaClO_3$....	*a*	47·10— 6·58	21·79—22·11	+0·008	H
Nitric acid	HNO_3.....	A	98·7 —43·1	16·22—16·81	+0·011	G
„ „	„	*a*	88·0 — 6·3	16·27—17·27	+0·012	H
„ „	„	„	41·0 — 6·0	17·08—17·32	+0·007	„
„ „	„	D	69·18—14·09	16·64—17·55	+0·015	Le Bl
Lithium nitrate.....	$LiNO_3$.....	*a*	42·18— 5·12	17·73—17·76	+	H
„ „	„	„	60·4 — 7·77	17·77—17·52	−0·005	„
Sodium „	$NaNO_3$	A	44·35—16·86	18·53—18·53	0	v.d.W.
„ „	„	„	42·9 —21·23	18·78—18·74	−	F
Potassium nitrate ...	KNO_3.....	D	17·55— 4·76	22·26—22·24	−	H
Cadmium „ ...	$Cd(NO_3)_2$..	„	54 03— 8 68	30·86—32·03	+0·026	de M
Silver nitrate	$AgNO_3$ ..	*a*	62·3 — 7·9	27·11—26·38	−0·013	H
„ „	„	D	44·5 — 5·88	27·11—26·6	−0·013	„
„ „	„	A	57·87—15·82	27·47—26·32	−0·028	F
„ „	„	*a*	21·3 —13·51	27·23—27·06	−0·021	Kan

TABLE IV (*continued*).

Substance.	Formula.	Line.	Change in strength, p_1 to p_2.	Change in molecular refraction, R_1 to R_2.	Average rate of change, $\frac{R_2 - R_1}{p_1 - p_2}$.	Observer.
Barium nitrate......	$Ba(NO_3)_2$..	α	9·87— 4·24	44·53—44·45	−0·017	H
Lead nitrate........	$Pb(NO_3)_2$..	A	31·65—14·27	52·43—51·21	−0 070	F
,, ,, ...	,, ...	D	35·94— 7·04	54·12—53·32	−0·027	H
,, ,, ...	,, ...	,,	34·6 —11·07	53·67—53·12	−0·028	,,
Mercurous nitrate...	$HgNO_3$....	α	21·22—13·86	35·87—36·11	+0·033	Ghira
Phosphorous acid....	H_3PO_3.....	D	73·69—30·66	21·29—22·09	+0·019	Zee
Sodium hydrate.....	$NaHO$.....	A	34·74—11·45	9·34— 9·31	−	v.d.W.
Ammonia..........	NH_3.......	,,	34·80—13·40	8·76— 9·03	+0·012	G
Sodium carbonate...	Na_2CO_3....	,,	16·30 — 9·32	21·33 —21·95	+0·089	,,
,, ,, ...	,, ...	α	14·25— 5·93	21·84—22·22	+0·046	H
,, ,, ...	,, ...	D	2·25— 0·095	22·56—22·72	+	Kl & Hl
Hydrocyanic acid ...	HCN......	,,	100·0 —33·33	10·19—10·21	+	B & B
Pot. selenocyanate...	$KSeCN$....	D	43·5 —32·8	41·83—42·31	+0·045	Zp.
Selenic acid	H_2SeO_4....	,,	41·8 —27·3	29·79—29·39	−0·027	,,
Selenious acid	H_2SeO_3....	,,	30·6 —23·0	26·98—26·84	−0·018	,,
Formic acid.......	H_2CO_2	α	83·64—63·01	13·97—14·07	+0·005	Lan
,, ,, ...	,, ...	D	29·06—18·69	14·02—14·00	−	Le Bl
Acetic ,, ...	$H_4C_2O_2$....	,,	100·0 —20·65	21·13—21·33	+	Lan
,, ,, ...	,, ...	,,	100·0 —10·81	21·14—21·39	+	Dam
,, ,, ...	,, ...	,,	5·2 — 0·057	21·45—21·45	0	Kl & Hl
,, ,, ...	,, ...	,,	100·0 —18·19	21·26—21·43	+	Le Bl
Propionic acid	$H_6C_3O_2$....	α	89·16—67·27	28·71—28·79	+	Lan
Butyric acid........	$H_8C_4O_2$....	,,	100·0 —47·85	36·22—36·10	+	,,
Trichloracetic acid ..	$HCl_3C_2O_2$ ..	D	30·11—14·13	47·66—47·72	+	Le Bl
Sodium formate... .	$NaHCO_2$...	A	44·99—41·39	16·60—16·63	+0·008	G
,, ,, ...	,, ...	D	8·72— 5·58	17·07—17·09	+0·006	Le Bl
,, acetate	$NaH_3C_2O_2$..	,,	45·89— 5·41	24·48—24·71	+0·005	,,

What are the conclusions to be drawn from this table?

1. It clearly and fully substantiates the old conclusion of one of the authors (Gladstone), that the molecular refraction of a dissolved salt or acid is the same, or nearly the same, whatever be the proportion of water.

2. It shows that differences unquestionably do exist in many instances, but to a smaller extent than between solids and their solutions. To illustrate this, we may take the first three substances in the list. Of hydrochloric acid, we have an experiment showing the change of molecular refraction from 14·54 to 15·12, or 4 per cent.; which is certainly far beyond the limits of experimental error. But this does not stand alone. It is supported by four experiments, made by two other observers with different apparatus, which give nearly the same ratio of refraction change, and always in the same direction, namely, that of increase. Moreover, an examination of the

whole data in Appendix I and Table I (p. 835) will make it evident that there is a gradual and fairly even progress from the lower to the higher figures as the strength of the solution is reduced. A similar deduction may be made from the observations on lithium chloride. With sodium chloride it is somewhat different; no series shows any very marked change, but the cumulative evidence leads distinctly to the conclusion that the sodium chloride is affected by dilution, in the same way as hydrogen and lithium chlorides, though not to the same extent.

3. The table shows not merely that in some cases at least there is a change on dilution, but that it has a chemical significance. This will be shown more fully in a subsequent section.

On comparing the conclusions in the two previous sections, it will be seen at once that there is a close coincidence, and that the effect of additional amounts of water is merely a continuation of the effect of water in first dissolving the salt or acid.

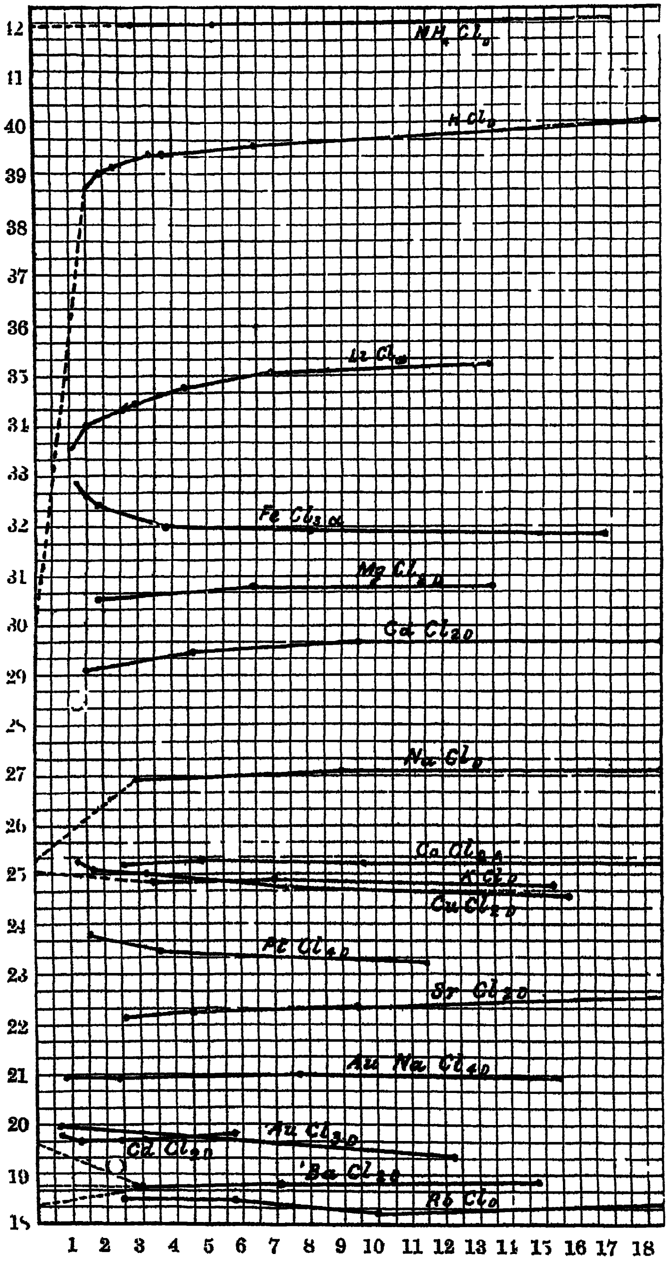
In both cases, we find that certain salts or acids exhibit a decided change, while the majority of them are not very clearly affected; those that show a marked increase in the one table, show a marked increase in the other, and *vice versâ*, and they appear in the same order.

This will become evident on a detailed examination of the tables, but will be better shown by the following diagrammatic arrangement. As, however, the molecular refraction in these previous tables involves the molecular weight, and as that is not of advantage for our present purpose, we have drawn out the results graphically upon the basis of the specific refractive energy of the salts instead of their molecular refraction, that is $\frac{\mu - 1}{d}$ instead of $\frac{\mu - 1}{d}P$. This has also the additional advantage that it is possible to bring our results together within more reasonable limits.

Another important change has also been made. Instead of plotting the percentage of salt in solution, we have transformed this into the weight of water for one part of the salt in each solution, and thus, the amount of salt being preserved uniform, we can see more clearly what is the actual effect on it of varying amounts of water.

In the diagrams, the ordinates represent the specific refractive energy of the salts or acids whether solid, liquid, or in saturated or weaker solutions. The abscissæ represent the proportionate amount of water, and the first that is plotted after zero indicates the specific refractive energy of the substance in saturated or nearly saturated solution. This is joined to the refractive energy of the anhydrous compound, but it must be borne in mind that the dotted lines are not intended to represent any continuous change in refrac-

DIAGRAM I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1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18
NH_4Cl_D
HCl_D
$LiCl_D$
$FeCl_3\alpha$
$MgCl_{2D}$
$CaCl_{2D}$
$NaCl_D$
$CoCl_{2A}$
KCl_D
$CuCl_{2D}$
$PtCl_{4D}$
$SrCl_{2D}$
$AuNaCl_{4D}$
$AuCl_{3D}$
$CdCl_{2D}$
$BaCl_{2D}$
$RbCl_D$

tion, but merely to connect the specific refractive energy of the solid salt with that of the same salt when it is dissolved in a minimum of water; from the nature of the case, there is no intermediate term. The continuous lines afterwards do represent the action of more and more water in modifying the refraction as revealed by the experiments.

The whole of the results might have been put on one very long diagram, but they would have interfered with each other, and it was thought more convenient and more instructive to break it up into four shorter and simpler diagrams, according to the nature of the compounds.

Diagram I gives chlorides.

Diagram II gives bromides and iodides.

Diagram III gives nitric acid and nitrates, to which have been added two other salts of analogous composition.

Diagram IV gives a series of sulphates, single and double.

A few substances are omitted from these tables, generally on account of shortness of range.

These four diagrams agree in showing clearly that the greater portion of a refractive change takes place in the passage from the solid or liquid to the dissolved condition. Where, however, this is

DIAGRAM II.

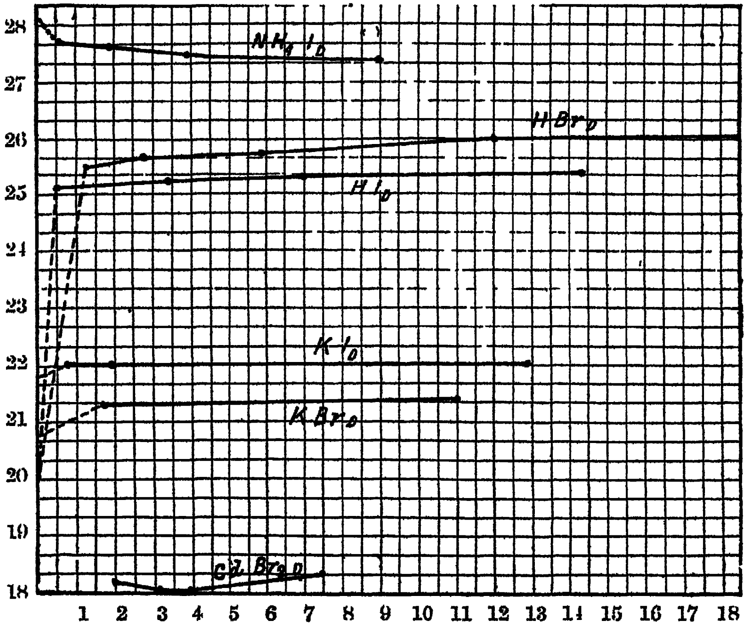
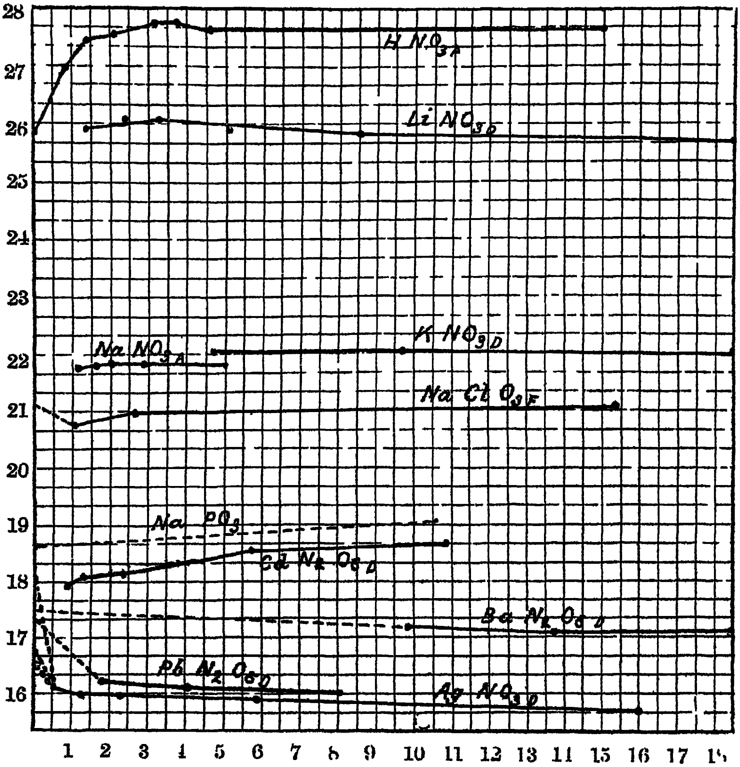
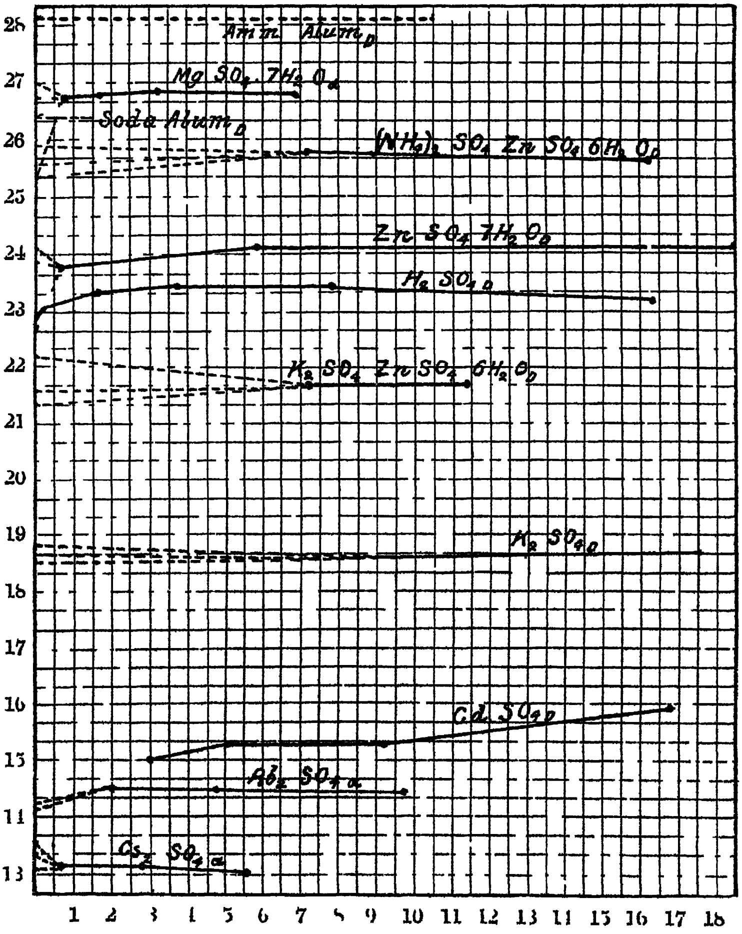


DIAGRAM III.



considerable the change is continued, as more and more water is added, in the same direction, but decreasing in amount, until in very dilute solutions it approximates to uniformity, and appears in the diagram simply as a straight line. In the majority of cases, however, this change on passing from the saturated to the weak solution is small, and in many cases it is scarcely perceptible. In that case it may be considered within the limits of experimental error. In another aspect, however, the curves exhibit a remarkable contrast. Generally speaking, the diagrams of the halogen compounds show a series of refraction changes by water, in the direction of increase; very large in the upper part of the diagram, but very small in the lower part. The diagram of the nitrates shows a moderate increase in the acid itself, but a striking decrease with the salts of the heavy metals, whilst the diagram of the sulphates is notable for an almost entire absence of any marked refraction change all along the scale.

DIAGRAM IV



If we study the diagrams more in detail, we observe the following facts.

Diagram I. *The Chlorides.*—By far the greatest refraction change is with the hydrogen compound, and we are able to observe that superiority, both in the difference between the anhydrous compound and the dissolved acid, and in the subsequent effect of different amounts of water. With the lithium salt, we have not the means of observing the change between the solid and the dissolved condition, but we may note the sharp curvature produced by successive dilutions. With the sodium salt, on the contrary, what we see is the great change on first dissolving, which of course cannot reveal itself as a curve, and which seems to have nearly exhausted the power of the salt to change in refraction through the further action of water. The potassium salt shows a very slight decrease, the rubidium is nearly constant. If we turn to the diatomic metals, the magnesium, calcium, strontium, and barium salts all show an increase on dilution, and so does cobalt. When, however, we turn to those salts in which more than two atoms of chlorine are joined with a metal, namely iron, gold and platinum, we have, on the contrary, a remarkable decrease of refraction on dilution.

Diagram II. *Bromides and Iodides.* These show a close analogy with the chlorides. The two hydrogen compounds show an action of water similar to that of hydrogen chloride, although not to so great an extent. The two potassium salts show an increase of specific refractive energy on passing from the solid to the dissolved condition, with no very perceptible change afterwards.

Diagram III. *Nitrates.*—Here again we find that the anhydrous acid when gradually mixed with water increases its refraction till it has combined with about four times its weight of water, after which it looks as though there were a slight decrease.

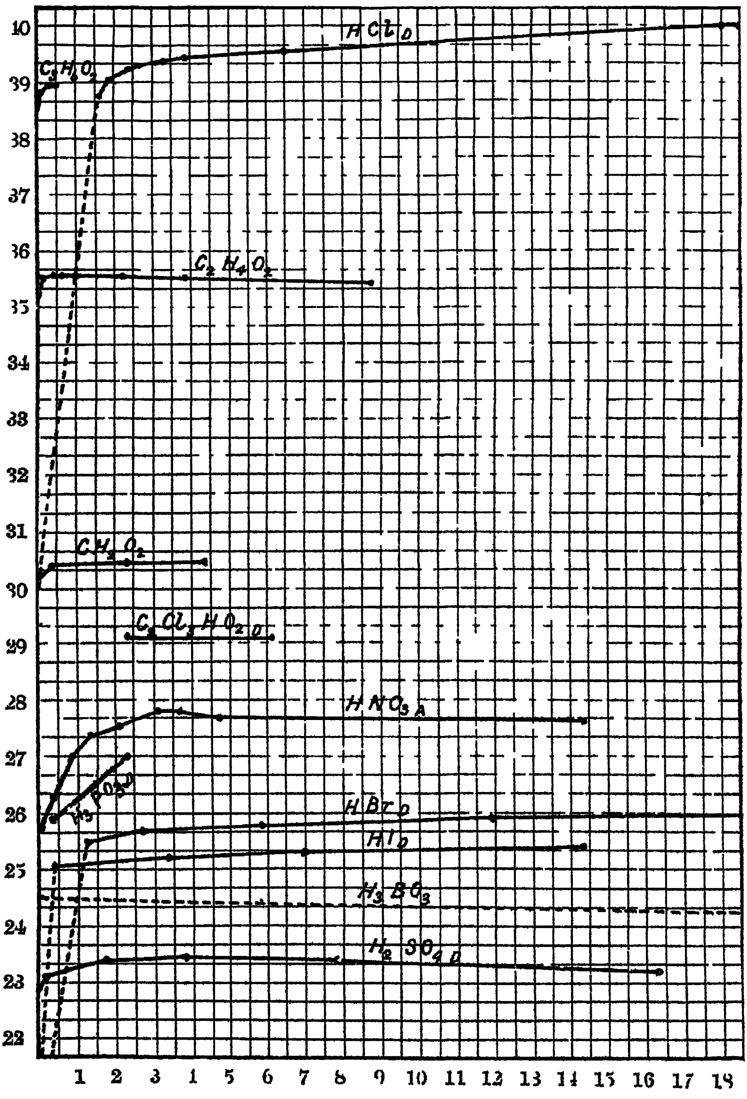
The lithium compound exhibits a similar kind of action, though to a much smaller extent. The sodium and potassium salts show little or no change through the continued action of water. The barium salt shows a decided decrease, and so do the lead and silver salts to a still greater extent.

Diagram IV. *The Sulphates.*—Hydrogen sulphate shows a close analogy to hydrogen nitrate, though to a smaller extent; a sudden rise when a little water is added to the anhydrous acid, a gradual curve upwards, and after that a slow decrease. The other sulphates generally show little, if any, change of refraction attributable to water, beyond the bringing of three indices of refraction into one, which is sometimes a little above and sometimes a little below the mean value of the three.

We have hitherto not referred to two striking exceptions, the cadmium and the ammonium salts. According to de Muynck's experiments, both the chloride and bromide of cadmium show at first a decrease of refraction, and afterwards a rather rapid increase. The two curves are very similar in form, and unlike any other on the halogen diagrams. The cadmium nitrate and sulphate show a rapid increase in refraction on dilution, in opposition to other salts of the same acid radicles. As the ammonium chloride heads Diagram I with practically a horizontal line, it is in striking contrast with its neighbour, hydrogen chloride, which shows the greatest amount of change. Ammonium iodide is also at the top of Diagram II, followed by hydrogen bromide and hydrogen iodide, and exhibiting a greater contrast, for it absolutely shows a decrease from both the initial and the subsequent action of water.

The following diagram, V, enables us to study the refraction change of acids in solution far better than we can in the separate diagrams, and to introduce observations on other acids.

DIAGRAM V



From this diagram, we see clearly the enormous change of refraction due to the action of water on the halogen acids, hydrogen chloride being far the most affected, followed by hydrogen bromide and hydrogen iodide. The next in order is unquestionably nitric acid; sulphuric acid is much lower. At a considerable distance come the organic acids. The difference in these is strikingly shown in the diagram by the horizontal line for acetic acid, which crosses the rising curve of hydrogen chloride. Yet there is a certain resemblance in the form of these curves. They show a quick rise at the commencement, then a rather sharp bend, and finally a horizontal line. The difference is mainly in proportion; the rise in the case of acetic acid is only about one twenty-fifth part of what it is in hydrogen chloride. The acetic acid has attained its maximum when it has mixed with about 1 mol. of water; the inorganic acids require very much more.

Formic acid shows a curve quite similar to that of acetic acid, and the short curve of propionic acid indicates a close resemblance. The short line of trichloracetic acid, is, as far as it extends, of the same form as that of acetic acid itself.

In the case of nitric, sulphuric, and acetic acids, there is, perhaps, a maximum, and then a slight descent.

Hydrofluoric acid has a specific refractive energy of only about 0·115, so that it could not be included in the present diagram. The portion of the curve hitherto examined does not show either rise or fall.

Effect of Change of Temperature.

We have already stated that any slight differences in the temperature of the solutions in Appendices I and II produces so small an effect that it may be taken as negligible.* Our principal experiments on this point were as follows. The figures in the last two columns are for the line α; MR and **MR** give respectively the molecular refractions by the old and by the Lorentz formulæ.

The different values for the molecular refraction of water at the different temperatures were taken into account in calculating out the results. It is evident that there is not much difference in refraction produced by the rise of 55°, or thereabouts, of temperature, especially with the stronger solutions. What small change there is seems generally to be in the direction of a fall at the higher temperatures. It must also be borne in mind that the difficulty of determining the refractive index at a particular temperature is greatly increased when that temperature is so much above that of the room.

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* Wüllner, long ago, practically showed this in his experiments on solutions of zinc chloride. Van d. Willigen also gives many observations on solutions at different temperatures.

Salt.	Per cent.	Temp.	M.R.	**M.R.**
Hydrochloric acid	21·1	23°·0	14·48	—
" "	—	77·0	14·29	—
" "	7·6	22·0	14·57	—
" "	—	77·0	14 22	—
Lithium chloride........	48·5	48·0	14·23	8·298
" "	—	80·0	14·25	8·261
" "	39·8	28·5	14·45	8·352
" "	—	74·2	14·48	8·376
" "	26·8	20·5	14·81	8·557
" "	—	82·5	14 84	8·572
" "	19·09	20·0	11·75	8·600
" "	—	75·0	14·65	8·545
" "	12·74	21·0	14·90	8·689
" "	—	77·6	14·76	8·619
" "	6·93	24·0	14·99	8·747
" "	—	75·5	14·76	8·591
Sodium chloride	26·41	21·5	15·68	9·126
" "	—	77·0	15·72	9·108
" "	8·32	22·0	15·84	9·250
" "	—	78·0	15·47	9·067
Magnesium sulphate. ..	21·85	22·0	24·05	13·607
" "	—	79·0	23·98	13·587
" "	7·9	23·0	24·13	13·590
" "	—	80·5	24·05	13·535
Cobalt chloride	26·35	21·0	33·20	18·989
" "	—	60·0	33·20	19·074
" "	10·59	18·0	32·29	18·398
" "	—	73·5	32·01	18·310

In connection with a possible change of refraction by change of temperature, the following experiment on solutions of sodium chloride at very low temperatures will be interesting. The columns speak for themselves. In determining the molecular refraction of the salt at the different temperatures, Damien's values for the refraction of water at those temperatures were taken.

Salt.	Per cent.	Temp.	M.R.
Sodium chloride	24·3	−6°·0	15·63
" "	—	−5·0	15·70
" "	—	−2·5	15·72
" "	—	−0·6	15·70
" "	—	+8·3	15·53
" "	9·1	−3·3	15·63
" "	—	−2·5	15·60
" "	—	−0·7	15·50
" "	—	+0·8	15·58
" "	—	+2·4	15·62
" "	—	+5·6	15·74
" "	—	+9·5	15·71

From these observations, it will be impossible to affirm that there is any variation in the refraction, either in the two different strengths or at the varying temperatures. There is also no indication of any particular change about zero or + 4°, the temperatures which have a special significance in the case of pure water.

Alternative Formulæ.

It may naturally occur to the reader that the small differences recorded in this paper may be due to the formula employed in the reduction of the experimental data, namely, $\frac{\mu - 1}{d}$; and that if the Lorenz formula $\frac{\mu^2 - 1}{(\mu^2 + 2)d}$ had been used instead, these differences might have become smaller or disappeared entirely.

Now, in cases where the refractive indices of the compounds compared differ widely, as in the comparison of gas with liquid, the two formulæ give very different relative results. But where the indices are nearly the same, as in the cases here examined, the two formulæ, though giving different absolute values, furnish very nearly the same relative results. We have occasionally thought it worth while to calculate out some of our data by the Lorenz formula, but have found that it did not affect the general conclusions. Instances of this are given in the preceding section on the effect of change of temperature.

The same remarks will apply to such modifications of this formula as have been suggested by Ketteler and others.

Analogies between Refraction Change and other Phenomena.

a. Refraction Change and Specific Refractive Energy.—The general relation is quite evident on a glance at the diagrams. In the upper part of the diagrams, where the specific refractive energy is greatest, there is the greatest increase on dilution. In the middle part, there is not much change, and in the lower part, the refraction decreases on dilution. There are exceptions to this, some of which will be afterwards considered.

The neutral zone between rising and falling change seems to be in about the same place with the chlorides, nitrates, and sulphates, say 20 to 24 on the scale of ordinates.

b. Refraction Change and Combining Proportion.—In 1870, it was pointed out that if those metals which form soluble salts be arranged in the order of their refractive energies, it will be seen that, with few exceptions, they are in the inverse order of their combining proportions—not their atomic weights, and that this "clearly points to some connection between the power of a metallic element to saturate the affinities of other elements, and its power to retard the rays of light," *Phil. Trans.*, p. 27.

In a lecture at the Royal Institution in 1877, this observation was somewhat extended, and it was shown that in regard to the univalent metals hydrogen, lithium, sodium, potassium, rubidium, silver, cæsium, and thallium, the specific refractive energy is, roughly speaking, inversely proportional to the square root of the combining proportion. The figures are not very exact, the specific refractive energy of sodium being too small.

Turning to the refraction change, we find it far the greatest with hydrogen, and in descending order come lithium, sodium, rubidium, potassium, and silver or cæsium, nearly the same as that given above. These belong to the first column in Mendeléeff's arrangement

If we turn to the second column, we find its members giving a refraction change which is considerable in calcium and in strontium and less in barium. In Mendeléeff's column 8, we have iron, gold, and platinum, each of which shows a decided fall.

In column 7 are contained the three halogens, chlorine, bromine, and iodine, while in our diagrams chlorine compounds show the greatest change, bromides showing somewhat more than the iodides.

Hence it appears that members of the same natural family of elements have special resemblances in regard to the property we are considering as well as in other respects.

This is further shown by the exceptional behaviour of ammonium chloride, which, although it stands at the top of Diagram I, and above hydrochloric acid, shows no change in refraction either on solution or dilution. It therefore is quite out of order with the chlorides of the univalent metals. But it must be remembered that ammonium is not a metal, although it plays the part of one.

c. Dispersion of Light.—It has been shown that variations in dispersion accompany variations in refraction, and it would seem not unreasonable to expect that if water should so modify a salt as to produce an increase or decrease in the refraction of one particular ray, it would produce a corresponding increase or decrease in the refraction of any other ray. If so, the change in specific dispersion, $\frac{\mu_H - \mu_A}{d}$, should be proportional to the change in the specific refractive energy of A or H, or any other line in the spectrum. It was observed, however, as far back as 1887, that the dispersion equivalents of the chlorides, bromides, and iodides of potassium and sodium in solution were greater than what the dispersion of other salts of the same bases would seem to warrant; and in 1891 very rapid advance in dispersion was clearly shown in regard to the halogen acids and nitric acid.

Our additional data afford some means of testing this, both on solid and liquid compounds as compared with the same substances in solution, as well as between different strengths of solution. It is evident, however, that to measure this change will require the best experiments and the widest range of lines observed in the spectrum. On the other hand, it may be remarked that the experimental errors are practically reduced to those which occur in measuring the two lines, as changes in strength of solution, density, or temperature are excluded.

In the following table, we give the molecular refraction and dispersion of two salts in the solid and the dissolved condition; sodium chloride, which shows the greatest rise on solution, and lead nitrate, which shows the greatest fall. In the case of sodium chloride, the molecular dispersion is reckoned for the A and H lines—$P\frac{\mu_H - \mu_A}{d}$; in the other case, we have only the data for the shorter range $P\frac{\mu_\beta - \mu_\alpha}{d}$.

	Sodium chloride.		Lead nitrate.	
	Mol. ref.	Mol. disp.	Mol. ref.	Mol disp.
Solid	14·6	0·86	56·60	2·45
Saturated solution.	15·6	1·13	53·14	2·10

In the case of sodium chloride, the increase in molecular dispersion between the solid salt and the salt in saturated solution is as much as 31 per cent., instead of the bare 7 per cent. shown by refraction.

In the case of lead nitrate, the decrease in the molecular dispersion is 14 per cent. instead of 6.

Our tables give little opportunity of judging of the change of dis-

Per cent. in solution.	Lithium chloride.		
	Mol. ref.	Mol. disp.	Ratio.
39·52	14·51	0·98	0·067
25·87	14·89	1·07	0·071
14·53	15·09	1·11	0·073
10·03	15·45	1·05	0·068

persion, as compared with the refraction change, at different degrees of dilution. The best instance is that series of lithium chloride in which the lines A and H are measured.

In this case, the dispersion seems to increase about *pari passu* with the refraction.

d. Magnetic Rotation.—It is well known that there is an analogy between the molecular refraction of a substance and its power of rotating the plane of polarized light. Now, as Dr. Perkin has determined the rotation of several acids and salts in aqueous solution at different strengths, we are able to test the question whether the analogy also holds good in this case.

In making this comparison, it must be borne in mind that Perkin gives his results for different percentages of the compound in solution, and it is for the molecular refraction that they are calculated out; hence his observations are comparable with our series as given in Table I, and Appendix I. The changes in molecular rotation have hitherto been found almost always larger in amount than the corresponding changes in refraction.

As to the halogen acids, Perkin shows that in the cases of hydrochloric, hydrobromic, and hydriodic acids, the molecular rotations found for the pure acids, first rise as the solution is diluted and then become practically stationary. It would appear, also, that the change is proportionally much greater with hydrochloric than with hydriodic acid, hydrobromic taking an intermediate position. All this agrees with what we find in the case of the molecular refraction of these acids in solution.

As to lithium chloride, Perkin remarks that aqueous solutions of this salt behave in a manner analogous to solutions of hydrochloric acid, and a comparison of the numbers given shows that the change is comparatively quite as great. Here, again, we have a close agreement.

In regard to sodium chloride, Perkin states that "in the presence of water, it does not increase in rotation to nearly the same extent as hydrochloric acid does." He shows, moreover, that the rotation of the salt when dissolved in water is much higher than when it is in the solid condition as rock salt. In both these respects, the refraction changes are of the same kind.

In the case of nitrates, on the contrary, there is an apparent discrepancy between the two phenomena. Nitric acid shows a very distinct decrease in rotation on the successive additions of water, whereas there is an increase in refraction, at all events till the strength is reduced to somewhere about 25 per cent. After this, the rotation is fairly constant.

With lithium nitrate, there is, at first, a decrease in rotation against the slight increase in refraction, but, afterwards, a slight decrease in both.

In the case of sulphuric acid, there is a steady, though small, decrease in rotation on the continued addition of water; whereas, in the refraction, there is a moderate increase at first, and, afterwards, a tendency to decrease. Both properties remain much more uniform on continued dilution of the acid than in the case of the halogen compounds.

Formic, acetic, and propionic acids in solution show no change by the further addition of water, either in molecular rotation or refraction. Here, again, therefore, we have a remarkable similarity.

Taking a broad view of the above summary, it will be seen that there is some correspondence, both when a change does occur and when it is absent.

Bearing on the General Question of Refraction Equivalents.

The results arrived at during this investigation explain to a considerable extent the difficulties experienced by one of the authors (Gladstone) in deducing the refraction equivalents of metals and other elementary substances from solutions of salts containing them. At the same time they point out improvements in the method of arriving at such equivalents. In the 1869 paper, it is said of the tabulated differences between long series of salts, they "are sufficiently near to show that we are dealing with a reality, but they are sufficiently wide apart to show that we must rely upon the average of the numbers, and not on any single experiment, if we wish to get a refraction equivalent true to the first place of decimals. Unfortunately all experimental errors fall upon this residuary number." The refraction equivalents arrived at independently by Kanonnikoff for many of the same elements by means of solutions do not exhibit a very satisfactory agreement with those just referred to.

This is not to be wondered at when we find that the refraction equivalents of many dissolved salts vary somewhat according to the strength of the solution, and may vary still more from that of the anhydrous salt, whilst at the same time other salts containing the same metal will not vary to a perceptible extent.

Attention was especially drawn in early days to the case of hydrogen in the halogen acids, which was stated to have an equivalent somewhere about 2·2 greater than in the organic acids, and intermediate values in nitric and sulphuric acids.

Again, in determining the actual value for potassium, which was the starting point for the metals in general, deductions from the chloride, bromide, and iodide were omitted, from the conviction that they gave values which were too high. Kanonnikoff went further, and, making no use of the haloid salts, he drew his conclusions solely from the nitrates, sulphates, and organic compounds of the metals. This difficulty is perfectly explained by the great influence which water exerts on these acids, and, to a minor degree, on most of their salts.

Now we are in a position to lay down the following principles which should guide in any future revision of these refraction equivalents where derived from salts. 1st, The anhydrous salt itself (or its hydrated crystal), when it can be obtained free from the influence of double refraction, should be taken in preference to its aqueous solution; 2nd, if deductions are made from aqueous solutions, it should be ascertained whether there is any appreciable difference in refraction according to the amount of water. If not, it may be assumed that the dissolved salt has practically the same refraction as the anhydrous salt. If, however, there be a change, the calculation should be made from the strongest solution, and the direction and nature of the dilution curve will give a good idea as to whether the true value should be in excess or deficiency, and also some idea of how much.

In this way, no doubt, we shall arrive at much greater accuracy than has been hitherto attainable.

Bearing on Theories of Solution.

The course of this investigation has led us more and more to the conviction that we were not dealing with salts or acids merely liquefied by the solvent and diffused through it. The many forms assumed by this refraction change, their evident dependence on the chemical and electrolytic nature of the substances dissolved, and the fact that different parts of the spectrum are unequally affected in solutions of different strengths, can scarcely be explained on any other supposition than that we are dealing more or less with new substances, produced by the interaction of the salt and its solvent. We have been observing, in fact, a mixture, not of two, but of several compounds, varying in their relative amount according to the proportion of water added.

Under these circumstances, there is no improbability that the changing chemical composition of the solution should reveal itself by alteration in its effect on the velocity of light. No argument can be drawn from these phenomena against the correctness of the law that the specific refractive energy $\frac{\mu - 1}{d}$ of a substance remains the same notwithstanding great changes of physical condition, and that "the specific refractive energy of a mixture is the mean of the specific refractive energies of its constituents" (*Phil. Trans.*, 1870). On the other hand, the results afford abundant indications of the general correctness of the law.

It may therefore be fairly expected that the phenomena described will throw some light on the controversies of the day as to the condition of salts in solution. As to the nature of the changes which we have been watching, we have not been able to satisfy ourselves, and we feel that there are several questions which require fuller investigation. These questions include—

1. How far is this refraction change dependent on the solvent used?
2. How far is it an additive effect as between acid and basic radicles?
3. What is the meaning of the positive and negative change? Does it indicate opposing properties or is it differential?
4. Why does not dispersion change *pari passu* with refraction?
5. Is this refraction change confined to electrolytes?

There are, however, some points on which we are prepared to give an opinion.

The Hydrate Theory.—We have little doubt of the existence of hydrates in solution, but our experiments do not give any clear evidence of them. In hydrated crystals, the salt and the water of crystallisation have the same specific refractive energy as though they were not combined, and though we have looked for coincidences between probable hydrates in solution and changes of curvature in our diagrams, we have not found any that we could distinctly recognise.

Decomposition into Base and Acid.—It has been suggested that NaCl, for instance, is converted by H_2O into HCl and NaHO, more or less. Our results are opposed to this, for it is evident that such a reaction cannot take place with HCl itself. Yet the refraction change on dilution is evidently the same phenomenon in the case of NaCl, LiCl, and HCl, the acid, in fact, showing it most strongly.

Gaseous Properties.—Whatever may be the evidence from other sources that a substance extended through a large amount of solvent gradually assumes the properties of a gas, our experiments show that this is not the case with its influence on light. Our having employed the $\frac{\mu - 1}{d}$ formula, enables us to form some opinion on this subject. The specific refractive energy of a vapour or gas is appreciably less than that of the same substance in the solid or liquid condition. The values obtained for dissolved salts in no case show diminutions comparable with what would be obtained with vapours, while in most cases they are of an opposite order; that is, they increase instead of decreasing.

Electrolytic Dissociation.—There is no doubt that whether the views which have been advanced by van't Hoff, Arrhenius, Ostwald, and others are correct or not, they have served as a connection between many different physical and chemical properties of electrolytes. To this group of properties must now be added the refraction change here described, for hydrochloric, hydrobromic, hydriodic, nitric, sulphuric, formic, acetic, and propionic acids follow one another in the same order, and are of about the same relative magnitude as when we are dealing with electric conductivity or chemical affinity (Diagram V).

There is also a qualitative resemblance between the curves of specific refraction and of electric conductivity in the case of nitric and sulphuric acids, when they are plotted according to the percentage composition, but this matter requires more detailed observation, and we propose to return shortly to the subject.

We therefore reserve final judgment on the cause of this refraction change till our investigations have been extended.

Summary.

The general conclusion is that when a salt or acid dissolves in water, the law of permanency of specific refractive energy, notwithstanding change of physical condition, does hold good; but that in many, if not most, cases there is some circumstance which causes a slight departure from it, while with the "strong acids" the departure is very considerable. This change takes place principally in the initial stage of solution of the solid or liquid compound, but in many cases a small further change is discernible as more and more water is added, but this becomes inappreciable as a balance is arrived at. This change in some cases is in the direction of an increased refraction, especially in the haloïd salts and the acids; in other cases, especially the nitrates and salts of low refractive energy, the change is in the opposite direction.

In either case, the dilution effect is in the same direction as that due to solution. In a few cases, where the dispersion was capable of being estimated, the change in it was proportionally greater than the change in the refraction itself.

The origin of this refraction change is at present obscure; but it probably arises from some gradual change of arrangement in the constituents of the salt or acid under the influence of water; and there are clear indications of some connection between the amount of this change and the amount of the specific refractive energy of the salts themselves, and also their combining proportions. It stands also in some relation to the phenomena of electric conductivity, and especially to those of the magnetic rotation of polarised light.

APPENDIX I.—*Molecular Refraction of Salts in Solution, previously published, or calculated from the Refractive Indices of Solutions given by various observers.*

Salt.	%.	Line.	R.	Obs.
HCl	36·09	F	14·54	G*
"	31·26	"	14·63	"
"	28·73	"	14·69	"
"	25·40	"	14·77	"
"	20·32	"	14·82	"
"	16·71	"	14·94	"
"	10·42	"	15·13	"
"	8·67	"	15·20	"
"	5·13	"	15·12	"
"	24·36	D	13·95	Le Bl
"	7·45	"	14·47	"
"	1·2	"	14·44	Kl & Hl
"	0·601	"	14·44	"
"	0·05	"	14·49	"
"	0·025	"	14·57	"
LiCl	40·0	red	14·42	Kr & Br
"	24·5	"	14·76	"
"	11·72	α	14·83	Weg
"	9·11	"	14·38	"
"	5·81	"	14·82	"
NaCl	26·14	red	15·66	Kr & Br
"	15·04	"	15·63	"
"	23·23	A	15·33	G
"	21·31	"	15·48	"
"	18·84	"	15·26	"
"	16·88	"	15·32	"
"	15·29	"	15·47	"
"	13·98	"	15·43	"
"	12·87	"	15·55	"
"	11·93	"	15·51	"
"	11·11	"	15·37	"
"	8·73	"	15·30	"
"	20·58	"	15·56	v d W
"	22·78	"	15·56	"
"	21·69	"	15·56	"
"	20·73	"	15 57	"
"	16·68	"	15·63	"
"	15·85	"	15·55	"
"	8·65	"	15·47	"
"	14·14	α	15·7	Bed
"	24·13	D	15·72	Le Bl
"	5·31	"	15·88	"
NaCl	21·73	α	15·70	Weg
"	23·63	"	15·71	"
"	22·40	"	15·73	"
"	21·37	"	15·73	"
"	16·57	"	15·76	"
"	7·99	"	15·76	"
"	25·0	α	15·70	Schütt
"	10·0	"	15·74	"
"	5·0	α	15·76	"
"	3·0	"	15·78	"
"	2·0	"	15·78	"
"	1·0	"	15·82	"
"	14·0	D	15·76	Hl
"	2·8	"	15·79	"
"	0·72	"	15·84	"
"	1·4	"	15·85	Kl & Hl
"	0·72	"	15·85	"
"	0·06	"	15·795	"
KCl	24·15	A	18·70	G*
"	21·62	"	18·77	"
"	17·15	"	18·60	"
"	12·12	"	18·60	"
"	9·92	α	18·97	Weg
"	7·40	"	19·07	"
"	4·99	"	18·95	"
$CaCl_2$	40·4	red	31·51	Kr & Br
"	24·75	"	32·01	"
"	40·64	A	31·89	v d W
"	31·79	"	32·02	"
"	24·38	"	32·00	"
"	16·75	"	32·06	"
$SrCl_2$	32·00	red	34·49	Kr & Br
"	19·93	"	34·46	"
$ZnCl_2$	71 81	α	31·32	Wull
"	57·40	"	31·27	"
"	47·87	"	31·56	"
"	35·90	"	31·56	"
"	46·08	A	30·52	G
"	41·43	"	30·69	"
"	35·25	"	30·63	"

* Series marked by an asterisk have been curtailed.

APPENDIX I—*continued.*

Salt.	%.	Line.	R.	Obs.
$ZnCl_2$	38·98	A	30·59	v d W
,,	31·50	,,	30·68	,,
,,	23·0	,,	31·03	,,
$CdCl_2$	57·52	D	36·09	de M
,,	41·55	,,	35·92	,,
,,	29·98	,,	35·93	,,
,,	14·78	,,	36·14	,,
NH_4Cl	24·83	A	22·19	v d W
,,	19·68	,,	22·18	,,
,,	14·51	,,	22·20	,,
,,	11·79	,,	22·14	,,
HBr	65·59	F	20·80	G
,,	56·00	,,	21·03	,,
,,	39·71	,,	21·17	,,
,,	24·60	,,	21·52	,,
,,	15·47	,,	21·83	,,
LiBr	9·28	α	21·05	Weg
,,	5·81	,,	21·01	,,
,,	4·02	,,	20·90	,,
NaBr	45·2	red	22·09	Kr & Br
,,	28·87	,,	22·27	,,
,,	31·02	α	21·83	Weg
,,	20·44	,,	21·88	,,
,,	11·96	,,	21·88	,,
,,	4·95	,,	21·89	,,
KBr	37·7	red	25·60	Kr & Br
,,	23·2	,,	25·53	,,
,,	19·82	α	25·17	Weg
,,	8·57	,,	25·21	,,
,,	5·01	,,	25·21	,,
$CaBr_2$	35·9	red	44·01	Kr & Br
,,	38·9	,,	44·78	,,
$SrBr_2$	48·56	,,	47·29	,,
,,	32·20	,,	47·21	,,
$BaBr_2$	50·50	red	53·07	,,
,,	33·60	,,	53·04	,,
$CdBr_2$	33·29	D	49·37	de M
,,	23·97	,,	48·78	,,
,,	20·55	,,	48·93	,,
,,	11·98	,,	49·75	,,
LiI	10·54	α	31·90	Weg
,,	5·90	,,	31·85	,,
,,	3·08	,,	31·88	,,
NaI	14·70	α	32·85	,,
,,	9·28	,,	32·93	,,
,,	6·25	,,	32·93	,,
KI	55·05	red	36·26	Kr & Br
,,	37·09	,,	36·48	,,
,,	55·12	α	36·06	Dam
,,	44·22	,,	36·31	,,
,,	39·70	,,	36·22	,,
,,	23·44	,,	35·54	,,
,,	18·70	,,	35·61	,,
,,	20·04	,,	36·17	Weg
,,	15·12	,,	36·14	,,
,,	10·27	,,	36·26	,,
,,	5·01	,,	36·29	,,
HNO_3	98·70	A	16·22	G
,,	69·60	,,	16·38	,,
,,	43·10	,,	16·81	,,
,,	69·18	D	16·64	Le Bl
,,	40·52	,,	17·19	,,
,,	28·66	,,	17·42	,,
,,	14·09	,,	17·55	,,
$NaNO_3$	44·35	A	18·53	v d W
,,	39·19	,,	18·52	,,
,,	33·89	,,	18·56	,,
,,	26·28	,,	18·52	,,
,,	16·86	,,	18·53	,,
,,	42·9	,,	18·78	For
,,	21·23	,,	18·74	,,
$AgNO_3$	37·87	,,	27·47	,,
,,	29·01	,,	26·89	,,
,,	15·82	,,	26·32	,,
,,	21·3	α	27·23	Kan
,,	13·51	,,	27·06	,,
$HgNO_3$†	21·22	,,	35·87	Ghira
,,	13·86	,,	36·11	,,
$Pb(NO_3)_2$	31·65	A	52·43	For
,,	14·27	,,	51·21	,,
$Cd(NO_3)_2$	54·03	D	30·86	de M
,,	43·72	,,	30·99	,,
,,	30·90	,,	31·06	,,

† Dissolved in very dilute nitric acid.

APPENDIX I—*continued.*

Salt.	%.	Line.	R.	Obs.
$Cd(NO_3)_2$ ...	21·35	D	31·44	de M
,, ...	14·90	,,	31·81	,,
,, ...	8·68	,,	32·03	,,
H_3PO_4	73·69	,,	21·29	Zec
,, ...	30·66	,,	22·09	,,
H_2SO_4......	94·72	A	22·36	v d W*
,, ...	91·43	,,	22·19	,,
,, ...	85·93	,,	22·27	,,
,, ...	71·97	,,	22·31	,,
,, ...	63·69	,,	22·54	,,
,, ...	56·25	,,	22·35	,,
,, ...	47·22	,,	22·48	,,
,, ...	38·78	,,	22·58	,,
,, ...	23·29	,,	22·52	,,
,, ...	15·82	,,	22·33	,,
,, ...	94·33	,,	22·97	Hd & Ws
,, ...	88·10	,,	23·11	,,
,, ...	81·19	,,	23·25	,,
,, ...	73·51	,,	23·06	,,
,, ...	64·91	α	23·08	,,
,, ...	55·22	,,	23·17	,,
,, ...	44·22	,,	23·43	,,
,, ...	31·62	,,	23·50	,,
,, ...	17·05	,,	23·80	,,
,, ...	94·11	D	22·23	Le Bl
,, ...	79·68	,,	22·42	,,
,, ...	60·98	,,	22·50	,,
,, ...	35·77	,,	22·62	,,
,, ...	21·68	,,	22·74	,,
,, ...	10·10	,,	22·88	,,
,, ...	4·78	,,	22·82	,,
,, ...	2·35	,,	22·90	Kl & Hl
,, ...	1·77	,,	22·86	,,
,, ...	1·195	,,	22·76	,,
,, ...	0·60	,,	23·00	,,
,, ...	0·075	,,	23·39	,,
,, ...	0·050	,,	23·28	,,
,, ...	0·025	,,	23·0	,,
Na_2SO_4.....	10·51	A	26·20	v d W
,, ...	9·55	,,	26·28	,,
,, ...	8·8	,,	26·08	,,
,, ...	6·8	,,	26·14	,,
,, ...	14·10	,,	24·32	For
,, ...	7·19	,,	23·88	,,
,, ...	25·51	D	26·30	Le Bl
,, ...	6·46	,,	26·45	,,
,, ...	4·76	,,	26·23	,,

Salt.	%.	Line.	R.	Obs.
$MgSO_4$.....	1·47	D	24·14	Kl & Hl
,, ...	0·75	,,	24·12	,,
,, ...	0·63	,,	24·32	,,
,, ...	0·31	,,	24·26	,,
$ZnSO_4$	1·58	,,	27·10	,,
,, ...	0·79	,,	26·98	,,
,, ...	0·066	,,	27·12	,,
,, ...	0·033	,,	27·08	,,
Soda alum..	21·39	,,	241·2	G
Amm. alum.	8·83	,,	256·8	G
NaHO......	34·74	A	9·34	v d W
,, ...	18·5	,,	9·36	,,
,, ...	11·45	,,	9·31	,,
Na_2CO_3	16·30	,,	21·66	G
,, ...	13·77	,,	22·02	,,
,, ...	10·50	,,	22·18	,,
,, ...	9·32	,,	22·46	,,
,, ...	2·25	D	22·56	Kl & Hl
,, ...	1·13	,,	22·68	,,
,, ...	0·57	,,	22·52	,,
,, ...	0·095	,,	22·72	,,
NH_3........	34·80	A	8·76	G
,, ...	33·40	,,	8·95	,,
,, ...	21·40	,,	9·06	,,
,, ...	19·92	,,	8·88	,,
,, ...	13·40	,,	9·03	,,
KSeCN	43·55	D	41·83	Zp
,, ...	32·77	,,	42·31	,,
H_2SeO_4.....	41·8	,,	29·79	,,
,, ...	27·3	,,	29·39	,,
H_2SeO_3.....	30·6	,,	26·98	,,
,, ...	23·0	,,	26·84	,,
CH_2O_2.....	100·0	α	13·92	Lan
,, ...	83·64	,,	13·97	,,
,, ...	71·88	,,	13·96	,,
,, ...	63·01	,,	14·07	,,
,, ...	29·06	D	14·02	Le Bl
,, ...	18·69	,,	14·00	,,
$NaHCO_3$...	44·99	A	16·60	G
,, ...	41·39	,,	16·63	,,

* Series marked by an asterisk have been curtailed.

APPENDIX I—*continued.*

Salt.	%.	Line.	R.	Obs.	Salt.	%.	Line.	R.	Obs.
$NaHCO_3$	37·28	A	16·58	G	$C_2H_4O_2$	18·70	D	21·39	Le Bl
"	8·72	D	17·07	Le Bl	"	18·19	"	21·43	"
"	5·58	"	17·09	"	"	5 2	"	21·45	Kl & Hl
					"	2·7	"	21·43	"
$C_2H_4O_2$	100·0	α	21·13	Lan*	"	1·37	"	21·44	"
"	99·87	"	21·14	"	"	0·22	"	21·47	"
"	99·5	"	21·16	"	"	0·114	"	21·46	"
"	98·2	"	21·20	"	"	0·057	"	21·45	"
"	93·02	"	21·27	"					
"	86·96	"	21·29	"	$NaH_3C_2O_2$ ..	45·89	D	24·48	Le Bl
"	81·63	"	21·32	"	" ..	21·81	"	24·53	"
"	76·92	"	21·29	"	" ..	9·70	"	24·58	"
"	70·39	"	21·30	"	" ..	5·41	"	24·71	"
"	60·66	"	21·28	"					
"	50·82	"	21·30	"	$C_3H_6O_2$	100·0	α	28·62	Lan
"	30·82	"	21·33	"	"	89·16	"	28·71	"
"	20·65	"	21·33	"	"	80·44	"	28·74	"
"	10·38	"	21·24	"	"	73·27	"	28·78	"
"	100·0	"	21·14	Dam*	"	67·27	"	28·79	"
"	93·02	"	21·24	"					
"	86·96	"	21·34	"	$C_4H_8O_2$	100·0	α	36·22	"
"	72·73	"	21·33	"	"	90·72	"	35·77	"
"	62·50	"	21·29	"	"	83·02	"	35·76	"
"	51·81	"	21·23	"	"	76·52	"	35·76	"
"	30·77	"	21·33	"	"	47·85	"	36·40	"
"	20·72	"	21·27	"					
"	10·81	"	21·39	"	$C_2HCl_3O_2$ ..	30·11	D	47·66	Le Bl
"	100·0	D	21·26	Le Bl	" ..	14·13	"	47·72	"
"	40·38	"	21·45	"					

* Series marked by an asterisk have been curtailed.

APPENDIX II.—*List of Authorities referred to, with the Abbreviations used in the Tables.*

Bd & W	Bedson and Carleton Williams, *Brit. Assn. Report*, 1881, 155 (salts, solid and dissolved).
Bl..........	Bleekrode, *Proc. Roy. Soc.*, 37, 339 (liquefied gases).
Br	Brewster, *Ency. Britt.*, Optics (silver nitrate).
B & B......	Bussy and Buignet, *Ann. Chim. Phys.*, 1864, [4], 3, 231 (hydrocyanic acid).
Dam	Damien, *Ann. École Norm.*, 1881, [2], 10, 233 (acetic acid and potassium iodide).
Dus	Dussaud, *Arch. Sc. Genève*, 1892 (sodium chlorate).
F	Forster, *Arch. Sc. Genève*, 1878 (salts).
Ghira	Ghira, *Gazzetta*, 1894, 24, i (mercurous nitrate).
G..........	Gladstone, *J. Chem. Soc.*, 1865, 18, 108 (rock salt, &c.); *Proc. Roy. Soc.*, 1868, 16, 439 (salts, acids, &c.); *Phil. Trans.*, 1870, 160, 9 (salts and acids, &c.); *Phil. Mag.*, 1885 (alums); *J. Chem. Soc.*, 1891, 59, 589 (acids and salts). Gladstone and Dale, *Brit. Assn. Report*, 1863, 12 (solutions).

APPENDIX II—*continued.*

G	Gladstone and Perkin, *J. Chem. Soc.*, 1889, **55**, 750 (correspondence with magnetic rotation).
Hg	Haagen, *Ann. Phys. Chem.*, 1867, 131 (rock salt).
Hl	Hallwachs, *Ann. Phys. Chem.*, 1894, **53**, 1 (acids and salts).
Hd & W	Handl and Weiss, *Wien. Ber.*, 1858, 30 (sulphuric acid).
H	Hibbert.
	Janovsky, *Wien. Ber.*, 1880, **82**, 148.
K	Kanonnikoff, *J. pr. Chem.*, 1885, [2], **31**, 321 (potassium sulphate, &c.).
Kl & Hl	Kohlrausch and Hallwachs, *Ann. Phys. Chem.*, 1894, [2], **53**, 14 (density of solutions, &c.).
Kr & Br	Kremers and Beer, *Ann. Phys. Chem.*, 1857 (various salts).
Lan	Landolt, *Ann. Phys. Chem.*, 1862, **117**, 353 (organic acids).
Le Bl	Le Blanc, *Zeit. physikal. Chem.*, 1889, **4**, 553 (acids and their soda salts).
Mas	Mascart, *Compt. rend.*, 1878 (gaseous halogen acids).
de M	de Muynck, *Ann. Phys. Chem.*, 1894, [2], **53**, 559 (cadmium salts).
N	Newton, *Opticks*, 2nd Book, Part 3, Prop. 10 (rock salt).
	Perkin, *J. Chem. Soc.*, 1886, **49**, 777; 1889, **55**, 680; 1893, **63**, 57; 1894, **65**, 20 (magnetic rotation).
Perr	Perrot, *Arch. Sc. Genève*, 1890 (double zinc sulphates).
R	Rubens, *Ann. Phys. Chem.*, 1894, [2], **53** (sylvin).
	Schmidt, *Ann. Phys. Chem.*, 1859, **107**, 539 (salts).
Sch	Schutt, *Zeit. physikal. Chem.*, 1890, **5**, **4**, 349 (sodium chloride).
S	Soret, *Arch. Sc. Genève*, 1884, **12**, 553; 1885, **13**, 5; 1888, **20**, 517 (alums).
T & C	Topsoe and Christiansen, *Vidensk. Selsk*, 1873, **9**, 9, 625 (crystals).
Tut	Tutton, *J. Chem. Soc.*, 1894, **65**, 628 (sulphates of alkalis).
Weg	Wegner, Berlin, 1889 (haloïd salts).
v. d. W	v. d. Willigen, *Arch. Mus. Teyler*, 1868, **1**, 74 and 161 (sulphuric acid and other solutions); *Arch. Mus. Teyler*, 1869, **2**, 238 (acids).
Wüll	Wullner, *Ann. Phys. Chem.*, 1868, **133**, 1 (zinc chloride).
Zec	Zecchini, *Real Acad. Lincei*, 1893, **31** (phosphorous acid).
Zp	Zoppellari, *Gazzetta*, 1891, **24**, ii, 396 (selenium compounds).

LXXXVIII.—*Rate of Escape of certain Gases from Solutions of varying Concentration.*

By EDGAR PHILIP PERMAN, D.Sc.

ON exposing a solution of a gas to the air, the gas escapes more or less rapidly, the rate of escape depending on the pressure of the gas in solution, on the extent of the surface of the liquid exposed to the air, and on the rate of diffusion of the gas.

Suppose, now, a rapid current of air to be aspirated *over* the solution; the gas will escape much more rapidly than before, for the diffusion will always take place into fresh air.

Again, let a rapid current of air be aspirated *through* the solution; the rate of escape will depend in this case on the pressure of the gas in solution, on the surface area of the bubbles passing through the liquid in a given time, and on the rate of diffusion of the gas. The bubbles will vary in size, but the average surface area of the bubbles passing through in equal intervals of time will be the same. This case is quite analogous to the one last mentioned, and with a rapid current of air, the diffusion of the gas practically always takes place into fresh air.

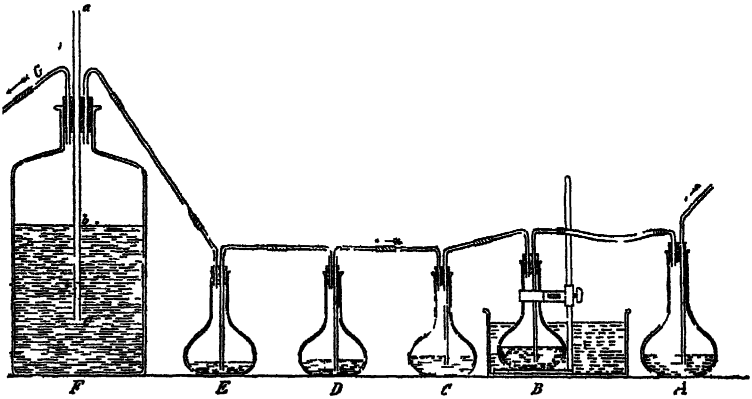
The method of experimenting is as follows. A rapid current of air is aspirated through the solution, and the amounts of the gas drawn off in given intervals of time, as well as the amount left in solution at the end of the experiment, are estimated, usually by a volumetric method. A curve is then drawn by plotting the amounts of gas (in grams) in solution, against the time (in minutes) during which the aspiration has been carried on. A series of tangents to this curve are then drawn at certain concentrations; the values of these tangents are the rates of escape of the gas at the concentrations selected.

The rate of escape of the gas will be proportional to the pressure of the gas in solution, provided that the other conditions of the experiment remain unaltered, as they do. The rates of escape are plotted against the corresponding concentrations, and in some cases the result is a straight line, that is, the rate of escape is proportional to the concentration, and therefore the pressure of the gas is proportional to the concentration, or the law of Henry holds good for the gas in question; in such cases the curve—amount of gas in solution against time—is that known as the logarithmic curve. The deviations from this law will be discussed later.

By this method we can therefore find the solubilities of a gas in a liquid at different pressures; the pressures being measured relatively to one another by the rates at which the gas is drawn off; the absolute pressures are not given by this method. The vapour-pressure of the solvent can be neglected.

Apparatus.—The apparatus employed consisted of a series of five wash-bottles, arranged as shown in the diagram (Fig. 1). A contained water, and served to make up any loss in B due to evaporation, and at the same time to purify the air passing through it. B contained the solution of the gas; it was immersed in a pan of water maintained at a constant temperature. C, D, and E contained water or some solution which would readily absorb the gas drawn off from B. Air was aspirated through the whole series of flasks by means of a water-air pump, and the constancy of the current was ensured by the arrangement, F. The pump was kept running at full pressure, so that air was drawn rapidly through the centre tube, *a*, *b*, *c*, which was ½ in. in diameter. The pressure in the upper part of the bottle was therefore always equal to the atmospheric pressure minus that of the column of water, *bc*. An experiment was conducted in the following manner. Air was drawn through the apparatus for, say, 5 minutes (the time being noted by an ordinary watch with a second-hand); the contents of the flasks, C, D, and E, were then washed into a stoppered bottle, replaced by fresh water or solution, and the aspiration carried on for another interval, and so on. At the end of the experiment the amounts of the gas which had been absorbed in C, D, and E were estimated, and also the residue in B. From the data obtained, the curve, Q, against *t* was constructed. The method of working will be best understood by the description of an actual experiment.

FIG. 1.



Aqueous Solution of NH_3.—Temperature, 16°. A solution was used containing 4·43 grams NH_3 in 50 c.c.; this quantity was placed in the flask, B, 50 c.c. water in C, 25 c.c. in D, 25 c.c. in E, and 86 c.c. in A. The aspiration was carried on during regular intervals of 15 minutes each.

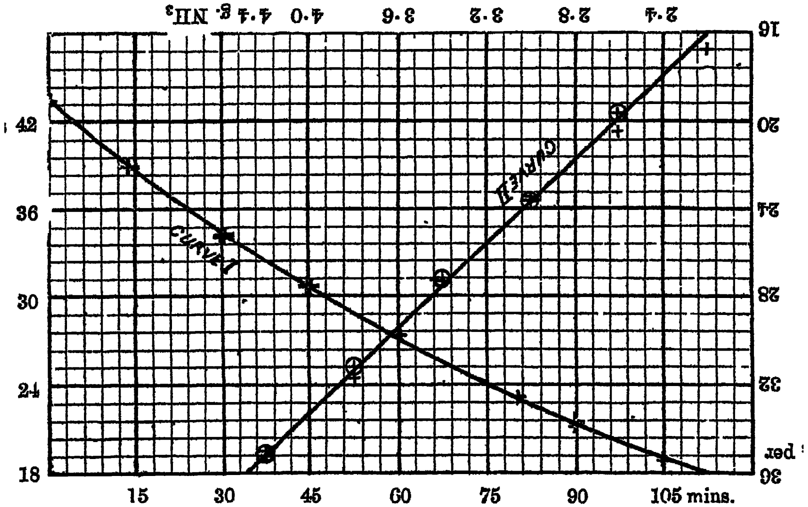
After each interval, the contents of the absorption flasks were transferred to a stoppered bottle, the flasks were recharged with the same quantities of water as before, the corks carefully adjusted to file-marks on the flasks, and the aspiration recommenced. The titrations were usually carried out at the end of the experiment by means of dinormal standard sulphuric acid solution, methyl-orange being used as indicator.

The following numbers were obtained.

NH_3 drawn off.	NH_3 in solution.	Time from beginning.
—	4·430 gram	0 mins.
0·5312 gram	3·899 „	15 „
0·4446 „	3·454 „	30 „
0·3853 „	3·069 „	45 „
0·3497 „	2·719 „	60 „
0·3906 „	2·329 „	80 „
0·1776 „	2·151 „	90 „
0·2521 „	1·899 „	105 „

By plotting the numbers in the second column against those in the third, Curve I, Fig. 2, was obtained. Tangents to this curve were carefully drawn at points on the curve corresponding to concentrations of 4·2, 3·8, 3·4, 3·0, 2·6, and 2·2 grams respectively in 50 c.c. of the solution, and the values were plotted against the amounts of ammonia in solution. The result is practically a straight line (Curve II, Fig. 2, points marked +). A second series conducted in exactly the same manner, gave points ⊕, which agree very closely with those of the first series; the divergence at small concentration is explained by the uncertainty of the tangents at the ends of the curve.

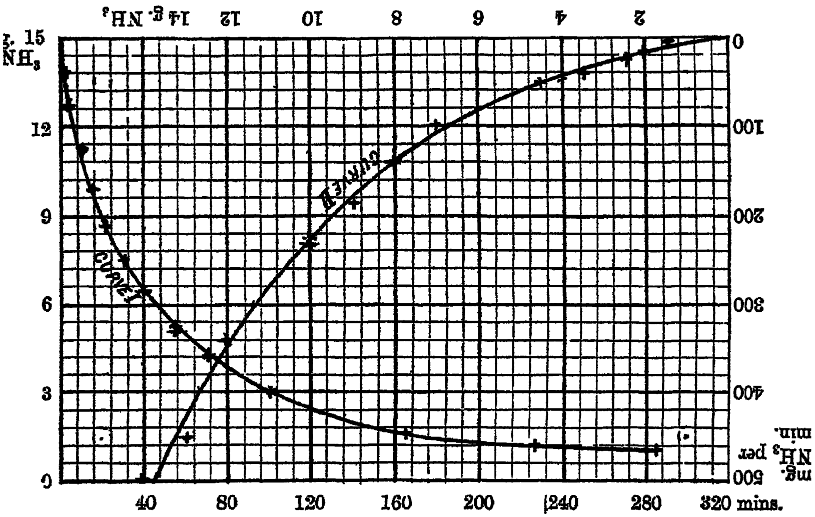
FIG. 2.—NH_3 solution.



The values of Q cannot be expressed by any simple equation.

As before explained, the values of the tangents are proportional to the gas-pressures, and therefore Henry's law appears from these results to hold good for ammonia between concentrations of 48 grams and 88 grams per litre. In order to test the validity of the law by this method, through the greatest possible range, concentrated ammonia solution was treated in a similar manner The Q t curve was quite smooth (Curve I, Fig. 3); it was re-drawn in two portions to ensure greater accuracy in drawing tangents, the values of which were then plotted on one curve (Curve II, Fig. 3). It is not straight, but deviates more and more from a straight line as concentration increases. The curve is, however, practically straight between any two points for which the concentration varies not more than 2 grams in 50 c.c.

FIG. 3.—Concentrated NH_3 solution.



Possible Errors.—The pressure of the ammonia in the concentrated solution was so great that during the intervals in the experiment, while the flasks were being washed out, it was found necessary to leave the flask B open at the outlet tube, otherwise the solution was driven rapidly up the long tube. An experiment was made to determine the amount of this error, and it was found by direct weighing that the loss of ammonia from the flask B containing concentrated ammonia solution, and left open at the outlet tube, was 0·02 gram in five minutes. The amount of ammonia drawn off, however, in the first five minutes was 2·4 grams. The error on the amount drawn off is therefore less than 1 per cent, and after one or two aspirations becomes inappreciable.

Another error is caused by the varying quantity of ammonia in the upper portion of the flask B. In order to discover the extent of this error, a flask of the same capacity as the aspiration flask (350 c.c.) was connected with the absorption flasks on one side, and with the aspiration flask on the other. After five minutes' aspiration through concentrated ammonia solution, the amount of ammonia in the new flask was estimated and found to be 0·118 gram. Now, at the beginning of the experiment, before the aspiration has commenced, there will be

	NH_3 in solution.	NH_3 in upper part of flask	NH_3 drawn off.
	s_1	f_1	0
and	s_2	f_2	d_1

after the first aspiration ;

now $\quad s_2 = s_1 - d_1 + f_1 - f_2 \quad \therefore s_1 = s_2 + d_1 - f_1 + f_2.$

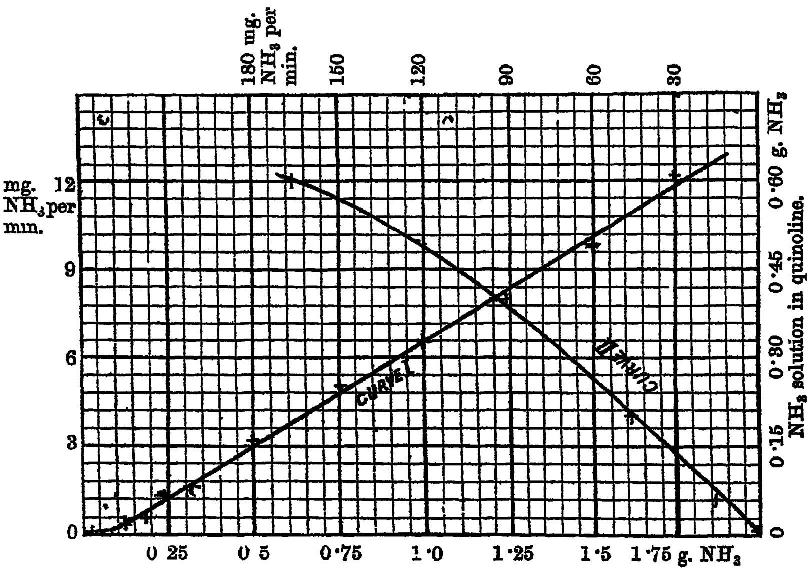
If there are n aspirations, the total error in s_1 will be $f_1 - f_n$. In the case in question, this amounted to about 0·1 gram, but the total amount in solution was 15 grams ; the error is therefore very small. The errors on the rates at which the ammonia is drawn off are much less than this.

A third error is caused by alteration of the concentration of the solution by evaporation during the experiment. The vapour-pressure of the water in B is less than that in A, owing to the gas dissolved in it, but the alteration is inappreciably small, for the whole amount lost by A in five hours was only 0·6 gram.

A dilute ammonia solution containing 2 grams of ammonia in 50 c.c. was also used. It gave for the tangent curve practically a straight line from a concentration of 1·75 grams to 0·1 gram of ammonia in 50 c.c. (Curve I, Fig. 4). Below this concentration, the line must make a curve in order to reach the zero point. This means that when the solution is very dilute, the attraction between the ammonia and the water is relatively greater than in stronger solutions.

NH_3 *Solution in Quinoline* (temp. 16°).—A solvent was sought for on which ammonia could have no chemical action. Quinoline was chosen as likely to fulfil this condition : 50 c.c. were saturated with ammonia, and treated in the same way as the aqueous solution ; quinoline also was substituted for the water in the flask A ; quinoline was found to be practically non-volatile for the purposes of the experiment. The solubility of ammonia in this liquid is very small compared with its solubility in water. The rate of escape curve, however, rises rapidly at the greatest concentrations in the same way as the aqueous ammonia curve (Curve II, Fig. 4). The formation of a hydrate may account for the enormously greater solubility of ammonia in water than in quinoline.

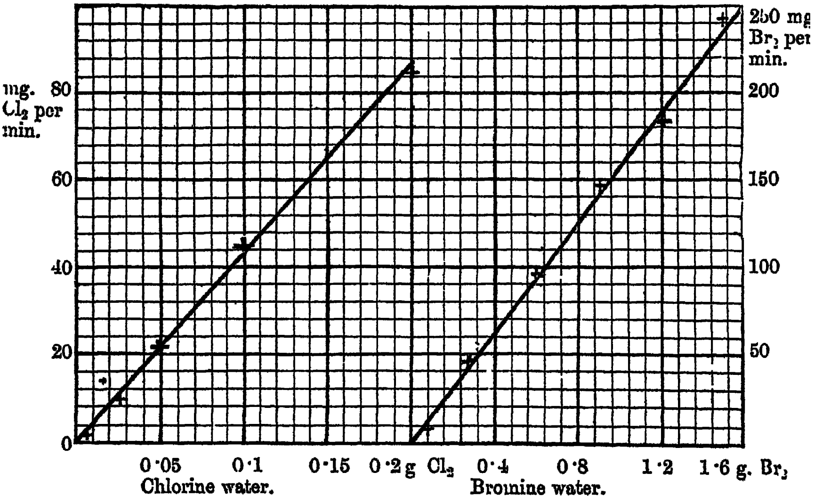
FIG. 4.—Dilute NH_3 solution.



Chlorine and Bromine in Water (temp. 11°).—In aspirating air through solutions of chlorine and bromine, the error caused by the gas remaining in the upper part of the aspiration flask, especially in the case of bromine, was found to be very considerable, owing, no doubt, to the great density of the gas, to the small amount which can exist in solution, and to the low rate of diffusion of the gas. This flask was replaced, therefore, by another, shaped like a distilling flask; the capacity of the bulb was but little more than 50 c.c., and the waste space was thus reduced to a minimum. The gases were absorbed by potassium iodide solution, which was titrated by means of standard solution of sodium thiosulphate. Chlorine is drawn off with great rapidity, and bromine somewhat less rapidly. The solution was entirely freed from the gas by half an hour's aspiration. The time intervals were necessarily very short: two minutes at the beginning and four or five minutes at the end of the experiment. The rate of escape curve is a straight line in each case (Fig. 5). Henry's law holds good, therefore, for these gases under the conditions of the experiment.

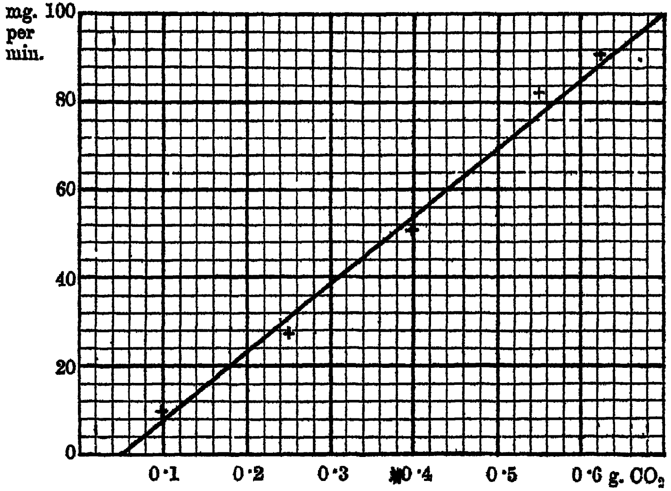
Carbon Dioxide in Water (temp. 11°).—An attempt was made to experiment on carbon dioxide in the same way, but the difficulties were found to be very considerable, owing to the sparing solubility of the gas, and to the impossibility of absorbing it in a potash bulb

FIG. 5.



without raising the pressure too much to be compatible with a regular current of air. The solution (400 c.c.) was placed in a 600-c.c. flask, and the loss of carbon dioxide on aspirating a slow current of air through it was found by direct weighing; the air being passed first through a U-tube containing calcium chloride and soda-lime. A calcium chloride tube was placed between the flask and the regulator, and was weighed together with the flask. The other flasks

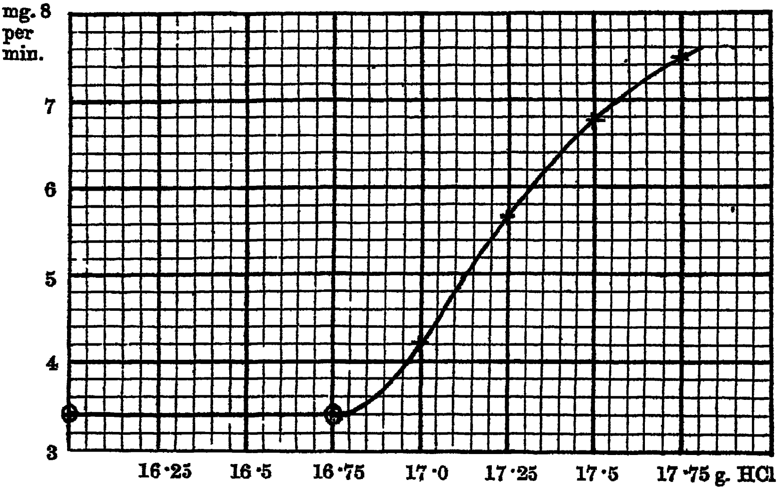
FIG. 6.—Carbon dioxide solution.



were not used in this experiment. The pressure-concentration curve appears to be a straight line, although the points are not very concordant (Fig. 6).

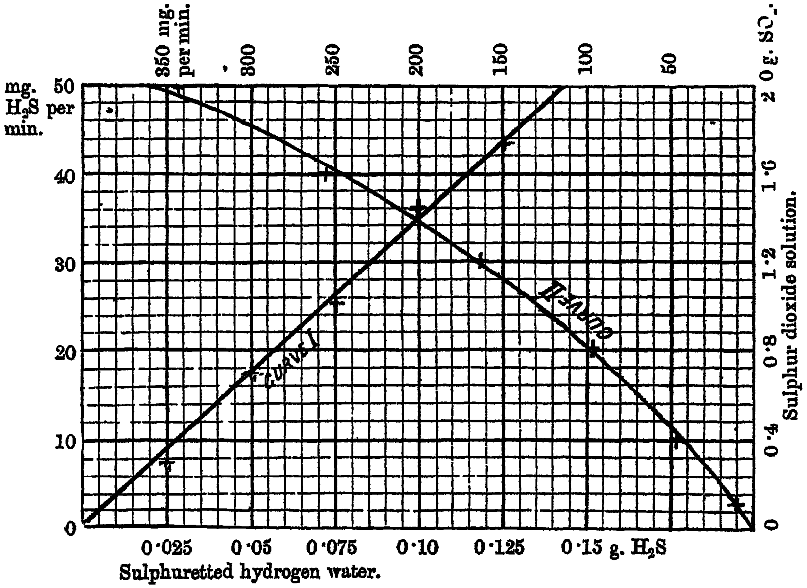
Hydrogen Chloride in Water (temp. 14°).—Pure concentrated hydrochloric acid was used; the gas drawn off was absorbed by water. The Qt curve is at first curved, but soon becomes straight, because, after 2½ hours' aspiration the acid distils over unchanged. The rate of escape curve is of a form entirely different from any of those given by other solutions; it shows a double flexure, and then becomes horizontal (Fig. 7). This gas is drawn off far more slowly than any other used, no doubt owing to the greater attraction it has for water; ammonia comes next in order of slowness.

FIG. 7.—Aqueous hydrochloric acid.



Sulphuretted Hydrogen in Water (temp. 12°).—A saturated solution was treated in the usual way, except that in order to prevent oxidation, a current of coal-gas was used instead of air. This was obtained by simply connecting the inlet tube of the flask A with a gas supply. The gas tap was carefully adjusted, and was then left untouched until the end of the experiment. The flask A contained dilute caustic soda solution to purify the coal-gas from any sulphuretted hydrogen that it might contain. The gas drawn off was absorbed by dilute caustic soda solution, and was estimated in the following manner:—The solution was diluted, acidified by hydrochloric acid, and an excess of standard iodine solution run rapidly in from a burette; the excess of iodine was then found by a thiosulphate solution. The gas is drawn off very rapidly, and 1 min. intervals were used at the beginning of the experiment. Henry's law is shown to hold good for this gas (Curve I. Fig. 8).

FIG. 8.



Sulphur Dioxide in Water (temp. 12°).—A saturated solution was treated in exactly the same way as sulphuretted hydrogen. The gas was absorbed by dilute soda solution, and titrated by a standard acid solution. It shows considerable deviation from the law of Henry (Curve II. Fig. 8). This confirms the results obtained by Sims (*Annalen*, 1861, **118**, 345), disproving those of Schönfeld, who came to the conclusion that this gas obeys Henry's law. The results of the experiments on ammonia, and hydrochloric acid confirm those obtained by Roscoe and Dittmar (*Annalen*, 1859, **112**, 349). These investigators employed much higher pressures than can be employed in the method now described.

The pressure of a gas in a solution saturated at the atmospheric pressure will be this pressure minus the vapour-pressure of the solvent, and this is the highest pressure available in this method.

The results obtained for carbon dioxide confirm those of Khanikoff and Luginin (*Ann. Chem. Phys.*, 1867 [4], **11**, 412), although they considered their work to disprove the law of Henry for this gas; but it has been pointed out by several investigators in this field of research that the deviations they found were caused only by experimental errors.

Summary and General Conclusions.—It has thus been proved by a new method that the law of Henry holds good for chlorine, bromine, carbon dioxide, and hydrogen sulphide, when dissolved in water, whilst ammonia, hydrogen chloride, and sulphur dioxide show large deviations from this law. These results confirm those of previous investigators. The less soluble gases, hydrogen, oxygen, nitrogen, &c., cannot be examined by this method; they were found to obey the law of Henry, by the discoverer of the law himself, by Bunsen, and others. On considering the behaviour of these various gases, it would seem very probable that the deviations from Henry's law shown by ammonia, hydrogen chloride, and sulphur dioxide, are caused by the formation of compounds of these gases with water; this idea is confirmed by the great solubility of each of these gases, and by the general chemical properties of the solutions. The departure from Henry's law cannot be explained by the approach towards the liquid state of the gases at the temperature employed. Bromine showed no deviation from the law at 11°. The actual constitution of the molecules of these gases in solution is a matter for further investigation.

TABLES OF NUMERICAL RESULTS.

Concentrated NH_3 Solution.

NH_3 in solution.	Time from beginning of aspiration.
15·19 grams	0·0 min.
13·79 ,,	2·5 mins.
12·70 ,,	5·0 ,,
11·03 ,,	10·0 ,,
9·82 ,,	15·0 ,,
8·79 ,,	20·0 ,,
7·47 ,,	30·0 ,,
6·41 ,,	40·0 ,,
5·17 ,,	55·0 ,,
4·24 ,,	70·0 ,,
2·97 ,,	100·0 ,,
1·72 ,,	165·0 ,,
1·27 ,,	225·0 ,,
1·078 ,,	285·0 ,,

Dilute NH_3 Solution.

NH_3 in solution.	Time from beginning of aspiration.
2·193 grams	0·0 min.
1·982 ,,	15·0 mins.
1·779 ,,	29·5 ,,
1·604 ,,	44·5 ,,
1·383 ,,	67·0 ,,
1·149 ,,	97·0 ,,
0·769 gram	157·0 ,,
0·523 ,,	217·0 ,,
0·366 ,,	277·0 ,,
0·196 ,,	398·0 ,,
0·099 ,,	578·0 ,,

Chlorine Water.

Cl_2 in solution.	Time from beginning of aspiration.
0·311 gram	0 min.
0·125 ,,	2 mins.
0·051 ,,	4 ,,
0·021 ,,	6 ,,
0·005 ,,	10 ,,
0·001 ,,	14 ,,

Bromine Water.

Br_2 in solution.	Time from beginning of aspiration.
1·882 grams	0 min.
1·325 ,,	2 mins.
0·973 gram	4 ,,
0·591 ,,	7 ,,
0·267 ,,	12 ,,
0·112 ,,	17 ,,
0·029 ,,	27 ,,

CO_2 Solution in Water.

CO_2 in solution.	Time from beginning of aspiration.
0·85 gram	0 min.
0·64 ,,	2 mins.
0·49 ,,	4 ,,
0·35 ,,	6 ,,
0·25 ,,	8 ,,
0·15 ,,	12 ,,
0·05 ,,	22 ,,

Aqueous Hydrochloric Acid.

HCl in solution.	Time from beginning of aspiration.
17·906 grams	0 min.
17·788 ,,	15 mins.
17·692 ,,	30 ,,
17·588 ,	45 ,
17·377 ,,	75 ,,
17·145 ,,	115 ,,
16·865 ,,	180 ,,
16·663 ,,	240 ,,
16·462 ,,	300 ,,
16·050 ,,	420 ,,

H_2S Solution in Water.

H_2S in solution.	Time from beginning of aspiration.
0·1898 gram	0 min.
0·1365 ,,	1 ,,
0·0975 ,,	2 mins.
0·0693 ,,	3 ,,
0·0489 ,,	4 ,,
0·0250 ,,	6 ,,
0·0051 ,,	11 ,,
0·0003 ,,	21 ,,

SO_2 Solution in Water.

SO_2 in solution.	Time from beginning of aspiration.
2·569 grams	0 min.
1·802 ,,	2 mins.
1·308 ,,	4 ,,
0·993 gram	6 ,,
0·600 ,,	10 ,,
0·372 ,,	14 ,,
0·156 ,,	22 ,,
0·071 ,,	30 ,,
0·020 ,	46 ,,

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LXXXIX.—*The Dissociation of Chloride of Gold.*

By THOMAS KIRKE ROSE, D.Sc., A.R.S.M.

THIS investigation was undertaken in order to obtain information as to the dissociation of trichloride of gold, and also to endeavour to explain the somewhat contradictory results already published by various experimenters on the relations between gold and chlorine. It has been repeatedly affirmed and denied that $AuCl_3$ readily volatilises, and the temperatures at which the chlorides of gold are formed and decomposed have also been variously stated by different observers.

In the course of the work, the pressure of dissociation of gold chloride at different temperatures up to 332°, and the effect on this pressure of the removal of all traces of moisture were observed. The volatility of gold trichloride in chlorine at various temperatures up to 1100°, and the rate of decomposition of both chlorides in air at various temperatures were also examined.

The first reference to the volatility of gold chloride appears to have been made by Robert Boyle, who describes experiments (*Philosophical Works of Robert Boyle.* Abridged by Peter Shaw, M.D., London, 1738, 1, 263 and 377) in which he and his assistants "dissolved gold in a moderate heat, with a sufficient quantity of the *menstruum peracutum* (which consists of spirit of nitre, several times drawn from butter of antimony), and having carefully decanted the solution into a retort, we very gently, in a sand-furnace, distilled off the liquor . . . . The liquor being abstracted, we urged the remaining matter by degrees of fire; and in no stronger an one than may easily be given in a sand-furnace, a considerable quantity of the gold would be elevated to the upper part of the retort, and would fasten itself to the top and neck in the form of a yellow and reddish sublimate. Sometimes we had the neck of the retort enriched with numerous large, thin, red crystals, very like rubies, and glorious to behold, which would run in the air *per deliquium.* Nor can I see any cause to doubt that, by the reaffusions of fresh menstruum upon the dry calx of gold which remains behind, the whole body of the metal may be easily made to pass through the retort." It should be noted that in this singularly interesting early experiment, the atmosphere inside the retort at the time of the sublimation must have mainly consisted of chlorine. Boyle also did not overlook the fact that these sublimed crystals could be shown to contain gold by various tests.

In the present century, but over 50 years ago, Mr. Lewis Thompson, in a paper read on November 1, 1838 (*Jour. Soc. of Arts*, 1840, **53**, part 1, 16), observed that his method of purifying gold "is founded on a circumstance long known to chemists, viz., that not only has gold no affinity for chlorine at a red heat, but that it actually parts with it at that temperature, although previously combined; that is to say the chloride of gold is reduced to the metallic state by heat alone [and] it cannot, therefore, possess any affinity for chlorine when red hot."

In a report appended to Mr. Thompson's paper by Mr. Arthur Aikin, who experimented on the same subject, it is stated that "in all the first trials the button of gold was found to weigh considerably less than before the process, and the accidental breaking of one of the tubes showed that in the part directly over the button several globules of gold adhered, having probably been thrown up thither by the ebullition of the alloy (of gold, with silver, copper, &c.) when the chlorine was first passed over it. Having thus discovered the cause of the failure, the process was twice more repeated, taking care to give only a low red heat in the beginning, and to pass the chlorine slowly. With these precautions, the button of gold remaining at the end of the process was found to be exactly equal to its original weight, as shown by a balance that indicated well to the 1/200th part of a grain."

In 1867, Mr. F. B. Miller (Trans., 1868, **6**, 506) described his process for the separation of silver and other metals from gold by means of a current of chlorine passing through the molten alloy, the success of the process depending on the extremely small volatility shown under these conditions by gold alloyed with silver. Roberts-Austen proved (*First Mint Report*, 1870, 93) that the presence of copper did not increase the loss of gold.

In 1868, Prat (*Compt. rend.*, 1870, **70**, 840) stated that if a current of gaseous chlorine is passed over any chloride of gold heated "suitably," a volatile chloride is obtained, which can be condensed and collected in the form of a liquid which contains more chlorine than does gold trichloride.

Experimenting on the same subject, Debray (*Compt. rend.*, 1869, **69**, 984) found that at 200° gold trichloride is decomposed with the formation of metallic gold and gold monochloride, and above this temperature with the formation of gold and chlorine. If chlorine is passed over gold leaf which is being gradually heated, then, as the temperature rises, the gold is covered with a coating of the chloride far below 300°; but it is not until a temperature of nearly 300° is reached that volatilisation of the chloride begins to be sensible. The volatilised chloride can be condensed in voluminous long needles in the cool part of the glass tube, the gold trichloride being kept from dissociating by chlorine vapour at atmospheric pressure.

In examining these statements in 1887, Krüss (*Ber.*, 1887, **20**, 211—213) obtained results which were considerably at variance with them. He placed precipitated gold, which had been dried at 180°, in a glass tube heated in an air-bath, passed a rapid stream of dry chlorine through the tube and heated it gradually, beginning at the ordinary temperature. At 140° to 150°, he observed the formation of red-brown fumes, a slight yellowish-red sublimate was formed, and the gold was converted into the red-brown auro-aurichloride, $AuCl,AuCl_3$. At 180° to 190°, this was decomposed, and greenish gold monochloride, $AuCl$, was left behind, and a little trichloride was volatilised. At 220°, the $AuCl$ was decomposed and a little trichloride was sublimed with the evolved chlorine; the sublimate consisted of shining reddish-brown needles, which were shown to consist entirely of $AuCl_3$. It was collected in a cool part of the tube and subsequently dissolved in water and analysed. On heating from 220° to above 300°, no further change was observed, and on cooling similar appearances were observed, in reverse order, at the same temperatures as before. From no less than one hundred repetitions of the process, only 0·12 gram of the trichloride, $AuCl_3$ was sublimed and condensed from a length of 30 to 35 cm. of the powdered gold. From these experiments, Krüss concluded that both Prat and Debray were mistaken in thinking that gold chloride is readily volatilised at moderate temperatures. He observed, however, (*Ber.*, 1887, **20**, 2641), that at 1100° continuous, though slow, distillation of gold chloride could be effected by passing a current of chlorine over metallic gold; he states that this sublimation begins at 1000°, although chloride of gold is completely decomposed at 220°.

Lindet subsequently (*Bull. Soc. Chim.*, 1888, **49**, 450) showed that while gold trichloride begins to dissociate into the monochloride and chlorine at 175°, the completion of the operation is slow, so that a stream of chlorine passed over metallic gold at 200° to 220° gives an ultimate product consisting of:

Gold in the state of $AuCl_3$	65·0	per cent.
Gold in the state of $AuCl$	13·5	,,
Gold not attacked	21·5	,,

Finally, S. B. Christy (*Trans. Am. Inst. of Mining Engineers*, May, 1888) in the course of an investigation into the causes of loss of gold in the chloridising roasting of auriferous ores, made a number of experiments on the rate of volatilisation of gold in a current of damp chlorine. He heated buttons of pure gold in clay dishes in a muffle furnace and passed a stream of chlorine through a pipe-stem, the bowl of which loosely covered the gold button. Under these circumstances the gold buttons always lost weight, the greatest loss being observed at 250°.

A. Smithells has lately shown (*Phil. Mag.*, 1895, **39**, 131) that "in presence of abundance of chlorine, gold chloride may be formed at a red heat, and so emit its characteristic spectrum."

It will be seen from these results how little the various statements confirm each other.

Pressure of Dissociation of Gold Trichloride.

The limited chemical action investigated is expressed by the equation $AuCl_3 \rightleftarrows AuCl + Cl_2$.

The chloride of gold was prepared by heating finely divided gold in a current of dry chlorine.

The chlorine was generated from hydrochloric acid and manganese dioxide in the earlier experiments, and from sulphuric acid, salt and manganese dioxide in the later ones, the formation of the gas being more easily regulated when obtained in this manner. The gas thus obtained was passed successively through three wash-bottles containing a solution of sulphate of copper to free the gas from hydrochloric acid and chloride of manganese, and was then dried by sulphuric acid and subsequent passage through some U-tubes filled with calcium chloride, and then through one filled with phosphoric anhydride. The P_2O_5 tube was added for the reason given by Krüss, who states (*Ber.*, 1887, **20**, 212) that a stream of gas, dried by sulphuric acid only, causes gold chloride to be completely dissolved. In the latter experiments, sulphuric acid only was used for drying the gas, two Winkler's tubes, and one U-tube filled with pumice-stone moistened by sulphuric acid being employed. The drying apparatus proved adequate for the purpose, as the current of gas passed through it had no apparent effect on dark-red anhydrous crystals of $AuCl_3$.

The purified and dried chlorine was tested at intervals by ascertaining to what extent mercury had power to absorb it. After agitation with mercury for fifteen minutes, the residue was usually about 5 per cent. of the original gas. In view of Shenstone's results (Trans., 1892, **61**, 449), it may be assumed that part of this residue was chlorine, but as no perceptible absorption of the residue by water could be observed, it is also probable that it consisted chiefly of air, the presence of which was of no moment.

The gold used was precipitated, washed, and dried at about 200° with the precautions observed in preparing the very pure gold used in the Royal Mint, in connection with the gold bullion assay, and was 1000 "fine." In the first series of experiments, the finely divided metal was dropped into the "gold chloride" tube shown in Fig. 1, and the tube then closed by the glass stopper, and heated at 180° in a slow stream of chlorine, which was at first completely absorbed. The chlorine was prevented from entering the manometer by the 3-way tap, which has a mercury cup and communicates with the "waste tube." The "gold chloride" tube was a little more than half filled by 1½ oz. of precipitated gold, the quantity usually employed. The resulting chloride was in the form of dark-red shining plates and needle-shaped crystals which consisted chiefly of gold trichloride, $AuCl_3$. Since the active mass of a solid is constant, it is immaterial what excess of AuCl may be present, provided that some $AuCl_3$ (indicated by its ruby colour) is also present.

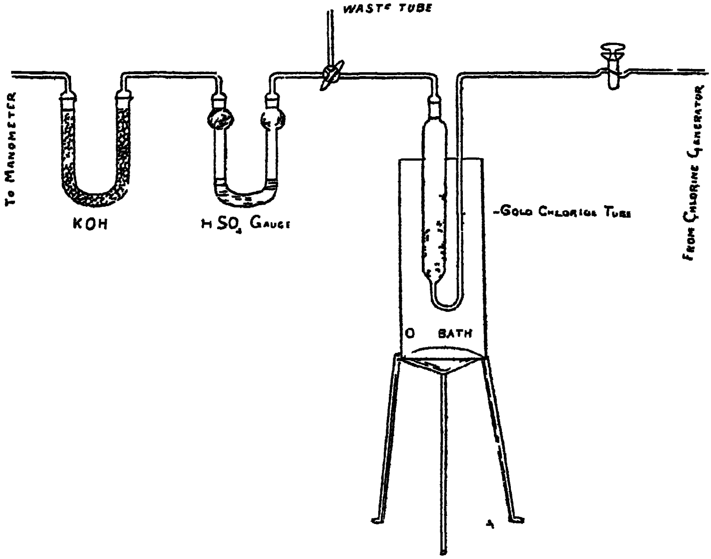


FIG. 1.—DISSOCIATION APPARATUS.

The chlorine contained in the chloride was enough to fill the tube (which is 10 ins. long and ¾ in. in diameter) many times over at atmospheric pressure. Only about four-fiths of the tube was heated in the oil bath, but this was of little consequence, as the pressure would be the same in different parts of the apparatus, although the composition of the gaseous atmosphere might be different. The thermometer used was a mercury one filled with nitrogen; its readings were subjected to the usual corrections.

The communication between the heated tube and the manometer was through two U-tubes (Fig. 1), one of which contained sulphuric acid to keep the chlorine from passing further and to act as a gauge, whilst the other contained solid potash to absorb such chlorine as might pass through the acid, and so protect the mercury of the Sprengel pump and manometer. It was found that 25 mm. of sulphuric acid above the mercury in the manometer was not enough of itself to protect it from the action of an atmosphere consisting mainly of chlorine, so that when the manometer was put in direct

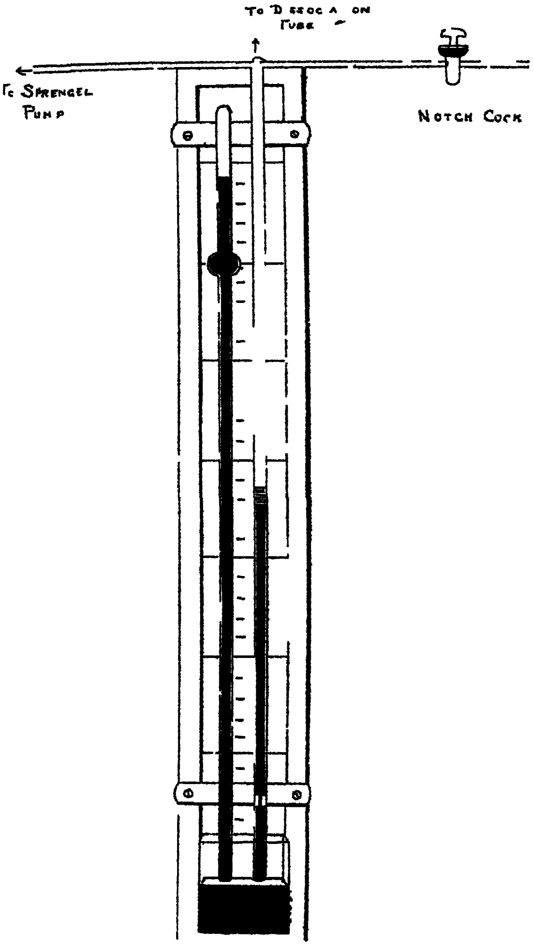


Fig. 2—The Manometer.

communication with the heated tube the results were not so exact. For very low pressures, the amount of sulphuric acid in the gauge was reduced to the smallest possible amount, but generally it was more convenient to keep about 30 mm. in each leg of the U-tube.

Measurement of the Pressure.—The arrangement of barometer and manometer, shown in Fig. 2, was suggested to me by Prof. Ramsay. Both tubes are furnished with air-traps, and the manometer and the upper part of the barometer are made from pieces of the same tube to avoid errors due to capillarity, whilst both dip into the same mercury vessel. These tubes are 12½ mm. in diameter. The graduated mirror placed behind and parallel to them is 3 ins. wide and 1 metre long, divided into millimetres, parallax being avoided by bringing the mercury and its image in a line with the eye. It is not difficult with this arrangement to read to the tenth of a millimetre with unassisted vision. The pressure inside the apparatus is the difference between the two readings. The correction for temperature—0·000173 lt.—had to be applied to this difference.

The upper part of the manometer tube opens into a 4-way tube, leading to the Sprengel, to the dissociation apparatus, and to the notch-cock (used to admit air) respectively. In place of the notch-cock an ordinary stop-cock and a fine capillary tube was used in some of the experiments.

For pressures above 760 mm. a U-shaped mercury manometer of ordinary form, having both limbs open above and graduated in millimetres, was used; in this case, the sulphuric acid gauge was dispensed with, the dissociation tube being put in direct communication with the manometer.

Method of Operating.—When a vacuum had been attained, the level of the sulphuric acid in the two limbs of the gauge was made the same, and kept so by the notch-cock and Sprengel during the progress of the heating. The oil-bath was heated to a definite temperature which was maintained until the pressure showed no further appreciable variation; this usually took place in about 20 minutes, but occupied a shorter time at high than at low temperatures. After taking readings, the Sprengel was started and the pressure reduced by from 10 to 20 mm.; the manometer was then again allowed to become stationary, so that if at any point the maximum pressure first observed was not restored it might be at once apparent. The temperature was then again raised and made constant, and a series of readings thus obtained. Finally the apparatus was allowed to cool, and the pressures again noted at various points; in general, these were higher than those noted with an ascending temperature, the differences being especially marked if the cooling had been rapid.

By slow cooling, however, and long waiting, readings only slightly higher than those previously recorded were obtained in some cases, so that the reaction seems to be completely reciprocating within the limits of temperature investigated.

The results obtained are given in the following table, and in the form of a curve in Fig. 3.

Temperature.	Pressure.	Temperature.	Pressure.
70°	0·0 mm.	218·0°	212 mm.
115	9·0	224·0	306
140	15·0	240·5	522
160	30·0	248·0	682
165	38·5	251·0	755
174	51·0	258·0	893
180	67·5	266·0	1021
191	98·0	273·0	1218
200	138·0	278·0	1354
207	161·0		

These are not single results, but the means of a number of fairly concordant ones. Other intermediate results were also obtained; for example, at 137° pressures of 15 mm. and 14·6 mm. were observed; at 138° a pressure of 14·8 mm.; at 139° a pressure of 14·7 mm; at 140° pressures of 15·7 and 15·3 mm.; at 142° pressures of 16·0 and 17·0 mm. From these results, the pressure of 15 mm. at a temperature of 140° is taken for the table and the curve.

The results, of course, show the maximum pressures corresponding to various temperatures when equilibrium is established. It must be noted that the pressures given are not the true pressures of dissociation, but the sum of the partial pressures p and p_1, where p = the pressure of dissociation, and p_1 = the vapour pressure of gold chloride.

The starting point of 70°, at which trichloride of gold is supposed to begin to dissociate, is somewhat arbitrarily chosen. At 66°, and at all lower temperatures, no pressure could be detected; at 74° the pressure is quite perceptible, but is less than 0·5 mm.; at 84° the rate at which chlorine is evolved in a vacuum is more than three times that observed at 74°, and the pressure is apparently between 1 and 2 mm., but the apparatus is obviously unsuitable for measuring very low pressures.

The observation of a pressure of 755 mm. at 251° is one in which special confidence may be placed, as this was confirmed several times, the temperature being on two occasions maintained for over three hours. Under these conditions attempts were made to obtain a sample of the gases in the hot part of the dissociation tube. For this purpose, the stop-cock leading to the chlorine generator was cut off, a partially exhausted flask was affixed by stout rubber tubing to the narrow tube leading from the bottom of the "gold chloride" tube, and the stop-cock of the flask was momentarily opened and then

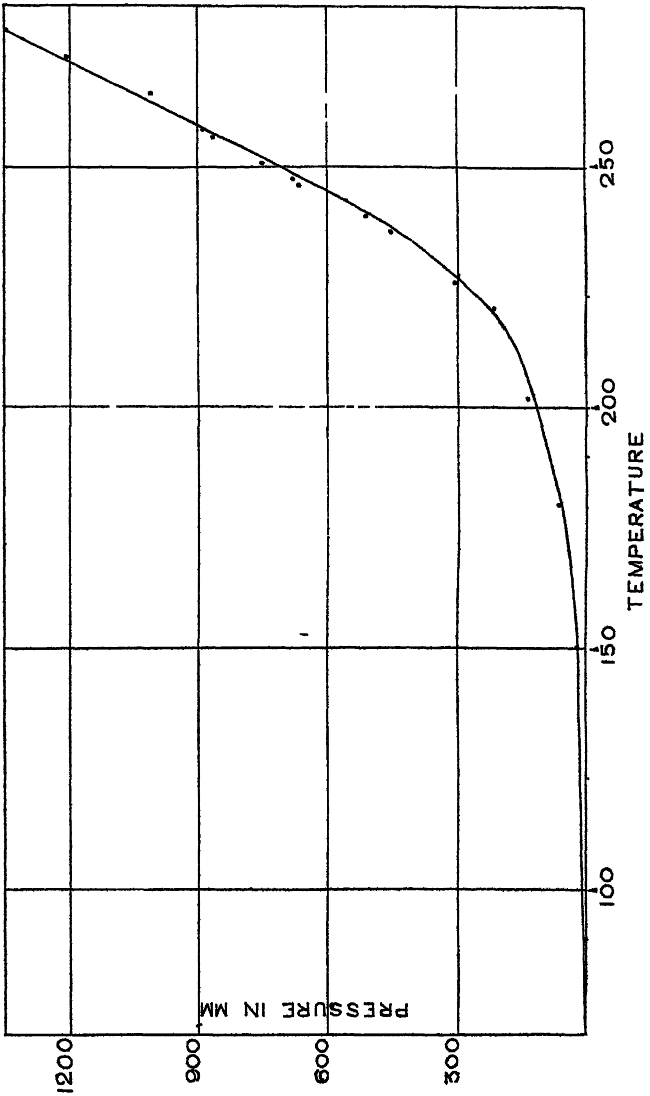


Fig 8

closed. It was hoped that by the rush of gas into the flask, any chloride of gold existing in the state of vapour would be carried over as dust, even if it were condensed by being cooled. It was assumed that this expectation was realised, and the flask was found to contain on one occasion 0 0537 gram of gold and 0·0919 gram of chlorine; and in the case of another experiment 0 0576 gram of gold and 0·1001 gram of chlorine. If the whole of the gold was present in the state of trichloride, as might be expected from Krüss's results, and those with the hot and cold tubes described below, this would correspond to the presence in the vapours at 251° of 1 mol. ($AuCl_3$) of gold chloride to about 3¼ mols. of chlorine.

These numbers are made use of in the calculations given subsequently (p. 893), by which the pressures of dissociation at different temperatures are theoretically deduced.

Experiments at Higher Temperatures.—In these experiments, the gold chloride was enclosed in the horizontal part, *a*, of a glass tube bent as in Fig. 4, and sealed at both ends. The part, *a*, containing the chloride was heated in an air bath; the bent part, *b*, was partly filled with sulphuric acid, and the internal pressure was observed by noting the compression of the gas in the part of the tube marked *c*. The whole tube was filled with chlorine and the sulphuric acid saturated with it before the ends were closed.

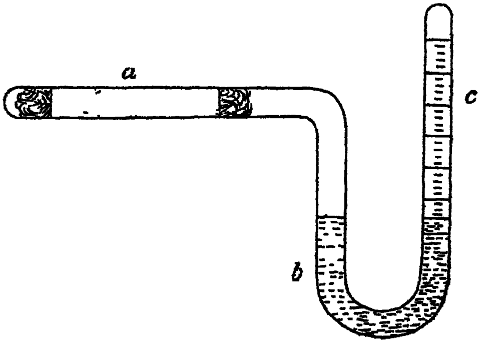


FIG. 4.

The results were as follows.

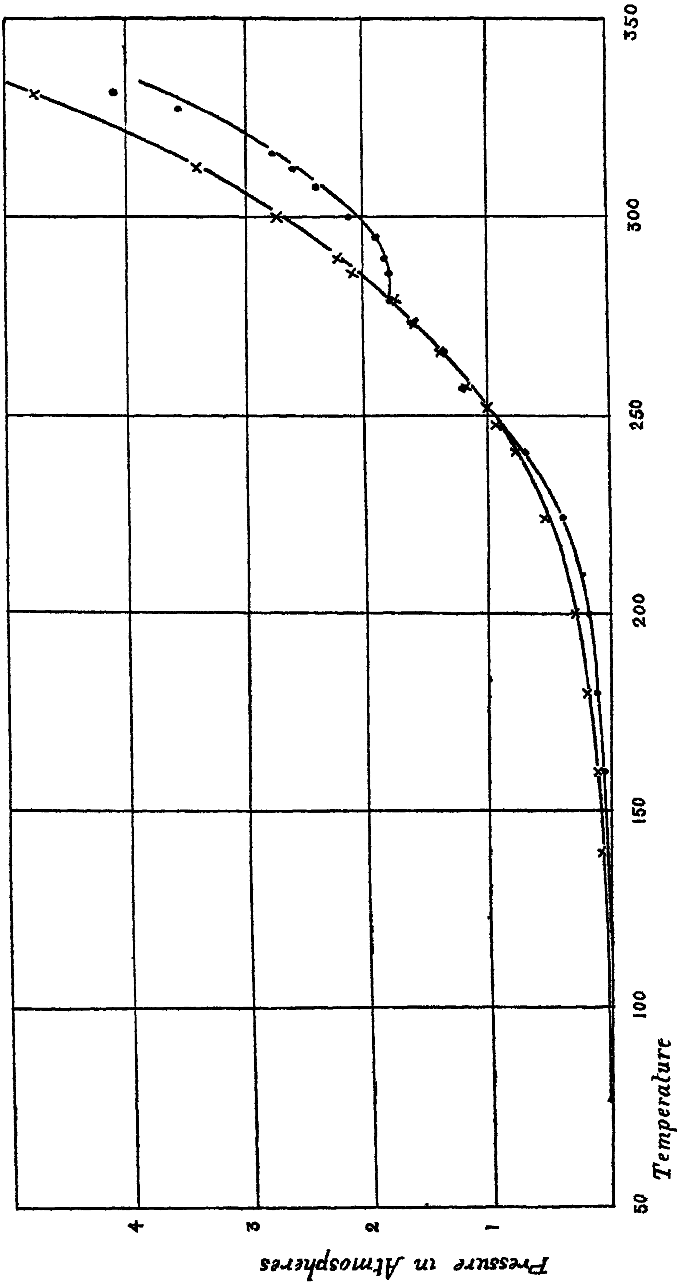

350
300
250
200
150
100
50
Temperature
4
3
2
1
Pressure in Atmospheres

Fig 5

Temp.	Pressure.
286° (the chloride now melting and bubbling)	1·81 atmospheres.
290	1·85 ,,
295	1·92 ,,
300	2·1 ,,
303	2·25 ,,
306	2 40 ,,
308	2·50 ,,
312	2·58 ,,
316	2·72 ,,
328	3·58 ,,
331	3·95 ,,
332	4·1 ,,

The accompanying curve, Fig. 5, shows both these results and those at lower temperatures. The dotted curve is obtained by calculation as explained below. It will be seen that while the agreement between the curves, obtained by observation and calculation respectively, is fairly close for all temperatures below the melting point of the chloride, the curves diverge above that point. This was to be expected, the constants being no doubt altered by the change in the physical state of the substance.

Calculation of the Pressure of Dissociation.—The pressure of dissociation can be calculated from the well-known formula

$$0·002 \log_e p + L/T = 0·0405$$

(given by H. le Chatelier, *Ann. des Mines*, 1888 [8], **13**, 211), in which p = pressure in kilograms per square metre; L = latent heat of dissociation (or of vaporisation); T = absolute temperature.

It is practically impossible to measure the latent heats of dissociation and vaporisation of $AuCl_3$ at the temperatures employed; these values can, however, be calculated approximately from the data obtained at 251° by using the equation given above.

Thus p (vapour pressure of $AuCl_3$) = 178/760 × 10333.
p'(tension of dissociation of $AuCl_3$ = 577/760 × 10333.
T = 524°.

By substituting these values in the equation, it is found that

L (latent heat of vaporisation) = 13·05 cals.
L′ (latent heat of dissociation) = 11·82 ,,

By substituting these values in the equation (and assuming them to be unchanged throughout the range of temperature within which the experiments were made), the results given in the following table are obtained.

Temperature.	Pressure in mm.			
	p.	p'.	$p + p'$.	
			Calculated	Observed.
70°	0·2	1·5	1·7	0·0
115	2·0	11·0	13·0	9·0
140	6·0	27·0	33·0	15·0
160	13·0	54·0	67·0	30·0
180	25·0	98·0	123·0	67·5
200	46·0	171·0	217·0	138·0
224	90·0	312·0	402·0	306·0
240	137 0	453·0	590·0	522·0
248	165·0	538·0	703·0	682·0
251	178·0	577·0	755·0	755·0
258	210·0	670·0	880·0	893·0
266	250·0	790·0	1040·0	1021·0
273	295·0	910·0	1205·0	1218·0
278	330·0	1000·0	1330·0	1354·0

Temperature.	Pressure in atmospheres; *i.e.*, values of $p + p'$.	
	Calculated.	Observed.
286°	2·1	1·81
290	2·2	1·85
300	2·7	2·1
312	3·4	2·58
332	4·8	4·1

The comparative want of agreement between the calculated and observed values of the total pressure at temperatures from 140—240° would be explained if the maximum pressures of dissociation had not been attained between these limits. The agreement, however, is much closer below the melting point of the chloride than above it, as has been already pointed out.

Effect of the Removal of Moisture on the Pressure of Dissociation.—The following experiments were made at the suggestion of Professor Armstrong, who thought it probable that perfectly dry chloride of gold would not show fixed pressures of dissociation, for the reason that dry chlorine would perhaps not combine with dry gold.

The tube shown in Fig. 6 was substituted for the one previously employed. The gold was placed in the tube and the latter then drawn out at *a*. The bulbs *b*, *b* contained P_2O_5, and the tube was

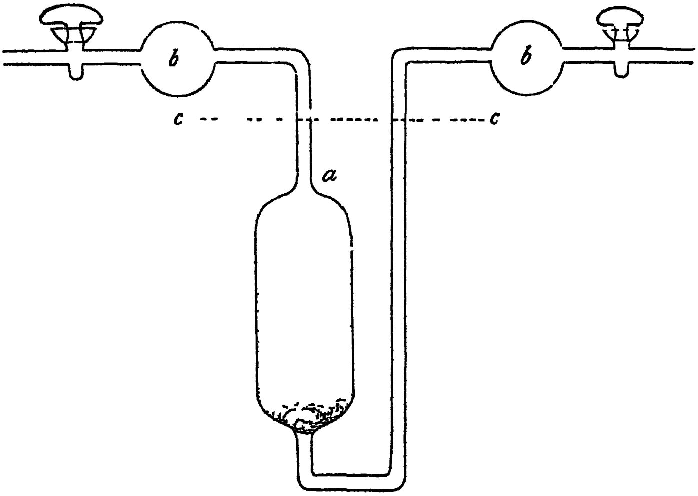


FIG. 6.

heated in the oil bath up to the line *c*, *c*. Gold chloride was then formed inside the tube as before, and the pressure of dissociation observed at a few temperatures, with the result that the previous values were confirmed. The tube was then exhausted and the vessel heated continuously at 180—200° during six weeks, some of the atmosphere of chlorine being pumped out occasionally. It was hoped that the traces of water contained in the gold chloride tube would be distilled off and be retained by the phosphoric anhydride. It was also expected that practically no moisture would pass through the sulphuric acid gauge, but even if it did, the air in the tubes on the other side of the gauge would also be eventually dried and the passage of moisture stopped. All the tubes were heated at intervals by a moving Bunsen flame. The pressures of dissociation subsequently taken were as follows.

After drying for 14 days.—

	Pressure.	
Temperature.	Dried chloride.	Undried chloride (from curve).
194°	86 mm.	108 mm

After drying six weeks:—

177·5°	42 mm.	59 mm.
204·0	101 "	150 "

The pressures given by the dried chloride were only reached after several hours heating, whilst those of the undried chloride were attained in less than an hour. The dryness of the chloride of gold seemed, therefore, to retard in a marked way the attainment of the maximum pressures of dissociation.

The question was then approached from the opposite direction. The gold chloride in the tube was heated to about 270°, and the vessel kept partly exhausted until no more chlorine could be removed. The exhaustion was then completed, the vessel allowed to cool, and filled with chlorine which had been in contact with phosphoric anhydride in a glass flask for six weeks. The transfer was made through a glass tube which had been exhausted, and then heated for some time; the stop-cock closing the flask was open for a moment only, when a rush of gas into the tube containing the gold took place, and the pressure in it was found to have been raised to over 600 mm.

The apparatus was then heated, and a rise of pressure occurred due to expansion of the gas by heating, until the temperature reached about 75° when the pressure began to diminish, although the rise of temperature was continuous. It was clear, therefore, that the chlorine was already being taken up by the gold. In half an hour from the time of introducing the chlorine, with the temperature at 220°, the pressure had fallen to 350 mm. The experiment was then stopped.

The result shows that carefully dried chlorine readily attacks gold. Shenstone has already shown that it attacks mercury when very dry (Trans., 1892, **61**, 451), and he suggested that the action of chlorine may be conditioned not so much by the presence of moisture, although it has a distinct connection with this, as by that of traces of other impurities.

Further investigation is required with perfectly pure dry chlorine, if it can be prepared, before the actions in which it takes part can be shown to take place according to Armstrong's theory of chemical change.

I am indebted to Mr. H. Brereton Baker for advice regarding the drying of the vessels and gases.

Experiments on the Volatilisation of Gold Chloride.

According to Krüss, gold can be volatilised in a stream of chlorine at 1100°, the action beginning at 1000°, although at 220° gold chloride is completely decomposed. Now both chlorides are formed at ordinary temperatures with evolution of heat, the heat of formation of dry $AuCl_3$ being given by Thomsen as 22·8 cals. at 15°, and being calculated from the results given above as 11·8 at 251°.

But according to the law of the displacement of equilibrium with temperature, given by van't Hoff (*Études des Dynamique Chimique*, 1884, 161, Amsterdam,), and subsequently extended by H. le Chatelier, every state of equilibrium between two different systems is displaced by a reduction of temperature towards that one of the two systems whose formation develops heat. It follows, therefore, that a compound in a state of equilibrium under constant pressure will be governed by the following laws.

a. If it is formed with evolution of heat, then the higher the temperature, the more complete the dissociation of the compound will be.

b. If it is formed with absorption of heat, then the higher the temperature, the greater the proportion of the compound that remains undissociated.

Moreover, J. Moutier had previously proved by means of thermodynamics (*Soc. Philomathique*, 1877, 3rd Series, **1**, 39 and 96) the following particular case of the law of the displacement of equilibrium: "When action takes place under a fixed pressure, only one temperature exists for which the reaction is reversible: below that temperature the reaction always takes place with disengagement of heat; above that temperature it takes place with absorption of heat" Here, as before, "reaction" stands for any change of physical or chemical state.

Moutier showed that this principle afforded a simple explanation of the fact cited by Troost and Hautefeuille (*Compt. rend.*, 1877, **104**, 946), that a number of compounds exist which can be formed at temperatures far above those at which they are decomposed, the only condition necessary to render the explanation valid being that these compounds should be endothermic. As a matter of fact, all the compounds cited, namely, silicon trichloride, chloride of platinum, ozone, oxide of silver, and several other bodies, are formed with absorption of heat.

It would appear, therefore, that, according to Kruss, gold chloride is an exception to the class of compounds which are re-formed at temperatures above those at which they are decomposed, and to the law by which their behaviour is explained. If Krüss were correct, then chloride of gold, on being heated, would dissociate more and more up to a certain point; then, on the temperature being further raised, a change (the recombination of gold and chlorine) would take place, which, by disengaging heat, would tend to raise the temperature still further, instead of tending to reduce it, as required by theory. Gold chloride would, therefore, belong to the same class of bodies as explosives, and the apparent equilibrium of the system below 300° would be one of "false equilibrium," such as is observable in a mixture of oxygen and hydrogen below 500°.

It might, therefore, have been expected, that Krüss was mistaken in believing that gold chloride cannot exist between 220° and 1000°. Professor Christy's results tend to strengthen that expectation, and it was hoped that by the use of "hot and cold tubes" the matter might be settled.

The apparatus just named was devised by H. Sainte-Claire Deville (*Leçons de la Soc. Chim.*, **4**, 316) and subsequently used by Troost and Hautefeuille (*Compt. rend.*, 1877, **84**, 946). The exact form used in the experiments now to be described is as follows. When the temperature used was not above 300°, a glass tube 1½ in. in diameter, containing 15 grams of finely divided gold placed in a porcelain boat, was heated in an oil-bath. The ends of the tube were closed with rubber corks, each provided with two holes; through one of these passed a little glass tube, serving for the introduction of a slow stream of dry chlorine, whilst at the other end a similar tube allowed it to escape. In addition, a thin tube of brass, coated with silver on the outside and 5-16 in. in diameter, was passed through the axis of the large glass tube; through the brass tube a rapid current of cold water was passed, and this was found to undergo no perceptible increase of temperature in passing through the apparatus. When the temperature of the oil-bath had remained stationary at the desired point for a few minutes, chlorine was introduced and passed over the gold for thirty minutes. The current of chlorine was then stopped, a rapid stream of dry air passed through until all the chlorine had been expelled, and the water then turned off, and the brass tube emptied and instantly withdrawn. After inspection, the tube was washed down into a capsule, and the washings analysed.

In the experiments at temperatures above 300°, the outer glass tube was replaced by one of glazed porcelain, and a thin glass tube 30 ins. long was used to convey the water, experience showing that it was perfectly safe and easier to wash clean. The temperatures were taken by the Le Chatelier pyrometer, the thermo-couple being placed close to the porcelain boat containing the gold. The couple was protected by being enclosed in a glazed porcelain tube sealed at the inner end, and placed inside the outer porcelain tube. The latter had its ends plugged with baked clay and sealed up, the arrangement of the tubes passing through the plugs being the same as in the other experiments described above.

The outer tube was heated in experiments Nos. 1, 2, and 3 (up to 300°) by an oil-bath; in experiments Nos. 4, 5, and 6 (up to 580°) in a gas furnace; and in the others (above 590°) in a coke furnace In every case, a length of about 20 in. of the tube was heated.

By the use of the "hot and cold tubes" a portion of the hot vapours is suddenly cooled below the temperature at which any change of chemical composition can take place; a sample more or less representative of the condensible vapours existing in the hot tube is thus preserved, and can then be examined at leisure. The outer surface of the water tube remains cool, the heating action to which it is subjected being mainly due to radiation.

The results obtained were as follows.

Number.	Temperature.	Gold volatilised.		
		Lost from boat.	Recovered from water tube.	Percentage volatilised in 30 minutes.
		grams.	grams.	
1	180°	—	0·00105	0·007
2	230	—	0·0522	0·35
3	300	—	0·3473	2·32
4	390	0·2731	0·1748	1·82
5	480	0·1325	0·0884	0·88
6	580	0·0907	0·0624	0·60
7	590	0·0864	0·0590	0·58
8	805	0·0753	0·0518	0·50
9	965	0·2441	0·1672	1·63
10	1100	0·2895	0·2037	1·93

For purposes of comparison, it may be added that when gold is heated in air or coal gas, no gold is volatilised below 1050°, and only about 0·02 per cent. in 30 minutes at 1100° (Trans., 1893, **61**, 717), or about one-hundredth part of that volatilised in chlorine.

In the table, the amounts "lost" by volatilisation include the amounts recovered from the water tube and the gold condensed on the inside of the outer tube; the latter sublimate was not recovered separately after each experiment.

In every case, the gold recovered from the water tube was associated with a little less chlorine than was required to form gold trichloride, and therefore presumably contained either some metallic gold or AuCl, or both; these doubtless resulted from the dissociation of some of the trichloride, when in the form of vapour.

The amounts volatilised vary according to two different factors. (1) The vapour pressure of gold trichloride, $AuCl_3$, which of course increases continuously as the temperature rises; and (2) the pressure of dissociation of the trichloride, which also rises continuously with the temperature, but not at the same rate as the vapour pressure. The rise of vapour pressure tends to raise, and that of the pressure of dissociation to reduce the amount of gold volatilised as chloride. The vapour pressure increases more rapidly than the pressure of dissociation at temperatures below 300°, and also above 900°, but less rapidly at intermediate temperatures. Hence the curve showing the

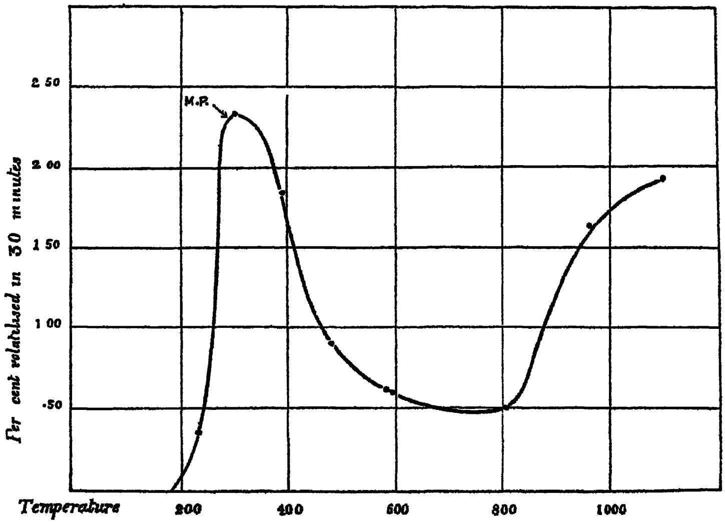


FIG. 7.

variation of volatilisation with temperature is irregular, passing through a maximum near 300°, and a minimum at a point somewhere below the melting point of gold. The first-named change in the direction of the curve possibly occurs at the melting point of the chloride, namely 288°. The second change is perhaps caused by the change of sign of the heat of formation of the trichloride $AuCl_3$; when this becomes negative, the pressure of dissociation of the compound would decrease, in accordance with the law of van't Hoff and Le Chatelier. However this may be, it is certain that when gold is heated in chlorine at atmospheric pressure, trichloride of gold is formed and volatilised at all temperatures above 180°, up to, and probably far beyond, 1100°.

It is thus shown to be improbable that gold chloride is an exception to the rule that a substance formed with evolution of heat exhibits a greater tendency to dissociate as the temperature rises. As already stated, several substances are known which, although they are completely decomposed at moderate temperatures, again become capable of formation at much higher ones, but these substances are all formed with absorption of heat. It is doubtful whether a substance formed by an exothermic change could behave in this way: for example, in spite of the results of C. Langer and V. Meyer (*Ber.*, 1879, **12**, 2202) on the behaviour of platinous chloride, which is stated to be capable of existing only below 300° and above 1300°, it is probable that its properties in this respect resemble those of gold chloride. This will be investigated subsequently by the "hot and cold tube."

Repetition of Kruss's Experiments.

As Krüss's results did not agree with those given above, it was thought desirable to repeat his experiments on the volatilisation of gold chloride (*Ber.*, 1887, **20**, 212). A glass tube was therefore filled with precipitated gold for a length of about 10 cm., and the empty part of the tube drawn out at several places. A slow current of chlorine, prepared as before, was then passed through the tube, and the part of the latter containing the gold gradually heated in an air-bath. The appearances noted by Krüss at temperatures below 180° were readily seen, but there was no further agreement with his observations. As the temperature rose higher, the sublimed crystals of chloride of gold formed more rapidly in the cool part of the tube, and the part which was being heated became darker in colour, until at 270° it was almost black, consisting of lustrous crystals, apparently composed of $AuCl_3$. At 285°, signs of decomposition of the chloride were perceptible, but even at 300° the rate at which dissociation was taking place seemed to be very slow. On cooling, the red colour gradually returned, and volatilisation became less by degrees. The stream of chlorine passing into the tube was, on the other hand, absorbed more and more, the greatest rate of absorption of the gas being observed at about 225°.

In a similar tube, but with a smaller quantity of gold, the rate of volatilisation at 260° was tested with a view to determine if it were really continuous. The following results were obtained.

Duration of experiment.	Amount of $AuCl_3$ sublimed.	
	Total.	Per hour.
1 hour	0·0926 gram	0·0926 gram.
3½ hours	0·3188 "	0·0911 "

The sublimation is thus seen to be perfectly continuous at 260°.

With regard to Krüss's observations, it may be noted that he made no attempt to ascertain whether the decomposition of either $AuCl_3$ into AuCl and chlorine at 180° to 190°, or that of AuCl into gold and chlorine at 220°, was complete at the temperature named. He trusted to inspection through the glass, although the thickness of the layer of gold in the tube was considerable. If the film next the glass were changed in the manner stated, the absence of change in the remainder would not be detected, and Kruss could thus merely observe the *beginning* of actions, which are incomplete until much higher temperatures are attained.

Rate of Decomposition of the Chlorides of Gold at Different Temperatures.

In this investigation, the method adopted was to heat a mixture of the chlorides of gold to various temperatures and for various lengths of time, (*a*) in the air, and (*b*) in an atmosphere of chlorine, and then to analyse the products. As pure dry chloride of gold, free from acids, is difficult to prepare in large quantity, a mixture of the chlorides was prepared as follows. One ounce of pure precipitated gold was heated in a stream of pure dry chlorine until no more was absorbed at 210—220°. The tube containing the gold chloride was then sealed up, heated to 300°, and the melted chloride shaken up, allowed to cool in a mass, and sampled. It was found to contain, by analysis,

Metallic gold..............	Nil.
$AuCl$......................	18·81 per cent.
$AuCl_3$....................	81·19 ,,

Portions were heated in porcelain crucibles in a water-oven and in an air-oven; the crucible being placed in a pipe-clay triangle supported on asbestos, and the bulb of the thermometer inserted in the crucible. In the "atmosphere of chlorine," the samples were placed in short glass tubes sealed up at one end and drawn out to fine capillaries about 7·5 cm. long, at the other; chlorine, generated by the decomposition of the chlorides, expelled the air from these tubes, and as long as the temperature was not allowed to fall, no subsequent entrance of air into them took place, except by diffusion, which would not be rapid under such conditions. Nevertheless, the pressure of chlorine in the bulb could not be expected to be quite equal to that of the atmosphere.

The results are given in the following table. The total weight of gold used in each experiment varied from about 0·5 to 2·5 grams. The chlorides were not weighed out at the beginning and the loss by volatilisation was neglected.

In addition to these experiments, some of the fused chloride was heated for seven days in an atmosphere of chlorine at 220°. The product, which was not analysed, consisted of two parts, a large quantity of volatilised dark red $AuCl_3$, in crystals, which were kindly examined and described by Mr. W. J. Pope (see succeeding paper, p. 906), and a residue, consisting, apparently, of a mixture of metallic gold and

Table of Experiments on Decomposition of Chloride of Gold.

Temperature.	Time of treatment.	Analysis of product. Percentages.			Percentage of $AuCl_3$ decomposed per hour.
		Metallic gold.	Gold as AuCl.	Gold as $AuCl_3$.	
In atmosphere of chlorine					
165°	4 hours	—	20·11	79·89	0·40
188	18 „	—	21·86	78·14	0·21
190	8 „	—	27·06	72·94	1·27
190	24 „	—	37·30	62·70	0·95
In air					
100°	7 days	—	24·33	75·77	0·04
165	4 hours	—	28·60	71·40	3·015
168	18 „	—	59·59	41·41	2·72
190	10 „	0·12	99·88	—	—
190	24 „	57·88	42·12	—	—
175—180°	6 days	100·00	—	—	—
155—163	7 „	52·23	47·77	—	—

gold monochloride, AuCl. The crystals of $AuCl_3$ did not change in appearance during the last five days, and seemingly were more stable than the $AuCl_3$ cooled from fusion.

The analyses were made, except in the last four cases, by digesting the product with ether, treating the residue with water, and estimating the gold in the two solutions and in the undissolved part. In the four cases mentioned, the preliminary treatment with ether was dispensed with, as the product was pale yellow and appeared to be free from the trichloride. The complete decomposition of the monochloride was ensured by digesting it with water for 48 hours, then gently warming it and washing the residue first with cold and then with hot water. The gold in solution was precipitated by sulphurous acid, and the chlorine estimated by precipitation as silver chloride. In every case, nearly 3 atoms of chlorine were found for each atom of gold in the portion soluble in water.

From the table, it is seen that $AuCl_3$, as it cools from fusion, suffers slow decomposition at as low a temperature as 165°, in an atmosphere consisting almost entirely of chlorine, and the decomposition is about five times as rapid if the temperature is 190°. In these experiments, the initial decomposition is much more rapid, as it takes place in an atmosphere of air until the latter has been driven out.

Gold trichloride, $AuCl_3$, prepared in a similar manner, is slowly decomposed in air at 100°, although not so rapidly as was observed by Lowe (*Ding. Polyt. Jour.*, 1891, **279**, 167) in the case of a solution of the trichloride; he states that 4 grams of gold trichloride, when heated in a porcelain basin on a boiling water bath, can be completely transformed into the monochloride, although not until after the lapse of several days. Monochloride of gold suffers slow decomposition in air at about 160°, and the decomposition is complete if it is heated at 175—180° for six days.

By making use of the formula $a_1/a_2 = (\tau_1/\tau_2)^m$, given by Harcourt and Esson (Bakerian Lecture, "On the Laws of Connection between the Conditions of Chemical Change and its Amount," read at the Royal Society, May 9, 1895), the following results are obtained. Taking the initial decomposition of gold trichloride in air at 165° as at the rate of 3·21 per cent. per hour, and at 100° as at 0·0411 per cent. per hour (the rates calculated from the first two experiments in air), the value of *m* for this chemical action is found to be about 27. Hence the rate of decomposition of gold trichloride should be about 0·365 per cent. in a year at 15°.

The value of *m* is about the same in the decomposition of gold trichloride in chlorine as in air. That is to say, the effect of temperature on the rate of decomposition of gold trichloride is about the same whether the latter is heated in air or in chlorine.

General Conclusions.

The results of the experiments prove that gold chloride shows fixed pressure of dissociation, the attainment of which is greatly delayed by very careful drying. The pressure of dissociation is insignificant below 70°, and becomes equal to that of the atmosphere at about 265°. As, however, the vapour pressure of $AuCl_3$, which is just perceptible at 100°, rises rapidly with the temperature, and becomes considerable between 200° and 300°, it follows that the pressure of dissociation combined with the vapour pressure of $AuCl_3$ is equal to that of the atmosphere at 251°.

The change of state of the chloride of gold from solid to liquid, which occurs at 288°, causes a decided check to be given to the rate of increase with temperature both of the pressure of dissociation and of the vapour pressure, but the greater effect seems to be produced on that of the latter.

The decomposition and volatilisation of gold trichloride take place in accordance with these properties. When the pressure of chlorine is kept constant at about 760 mm., the continuous volatilisation of $AuCl_3$ is readily observed at 180°, and increases rapidly until about the melting point. The rate of volatilisation then falls slowly as the temperature rises through several hundred degrees, but shows a minimum at about 800° and again increases, owing to the falling-off of the pressure of dissociation as compared with vapour pressure. Probably the heat of formation of $AuCl_3$ passes through zero and becomes negative at between 800° and 1000°. This could only be determined with certainty by calculation, using the specific heat of the substance, which is not known, and those of its elements. The change of sign of the heat of formation would readily account for a diminution in the pressure of dissociation, and consequent increase in the observed rate of volatilisation at high temperatures.

The decomposition of gold trichloride in air might be expected to become perceptible at 70°, requiring, however, about 25 years for its nearly complete change into the monochloride, AuCl, at this temperature. The observed rate of decomposition at 100° shows that a similar change would require about 1,000 days at this temperature, while it results from calculation, using Harcourt and Esson's formula, that at 200°, 36 hours, and at the melting point, namely, 288°, less than one minute suffices for the complete decomposition of $AuCl_3$ in air.

There might appear at first sight to be a discrepancy between the results obtained on the one hand by heating gold trichloride, and on the other by passing a stream of chlorine over metallic gold. In the former case, the pressure of dissociation becomes equal to four atmospheres at about 332°, and by the direction of the curve between 300° and 330° might be expected to become enormous at a bright red heat. Nevertheless, by the use of the "hot and cold tubes," gold trichloride is condensed from the stream of chlorine at atmospheric pressure at all temperatures between 180° and 1100°. The reason for this is partly to be found in the change of the heat of formation of $AuCl_3$ with temperature, but mainly in the extreme slowness with which the last traces of a compound are dissociated, even when it is much above its mean temperature of dissociation. This is, of course, attributable to the differences in the movements of the atoms in the different molecules in a given mass at a definite temperature. As already stated, there is reason to believe that at the ordinary atmospheric pressure, there is no temperature at which it is impossible to form gold chloride.

The Royal Mint.

XC.—*Some Physical Properties of the Chlorides of Gold.*

By Tom Kirke Rose, D.Sc., A.R.S.M.

Melting Point of Gold Trichloride.—In the course of the work described in the previous paper, it was found that gold trichloride could be readily fused if heated in a sealed tube, or under a pressure of two atmospheres of chlorine; the liquid was quite black and did not wet glass; some effervescence occurs as the chloride melts. The melting point was determined by heating about a gram of pure, dry volatilised gold trichloride in a sealed tube in sulphuric acid; three determinations were made, each of which gave the melting point as 288°, a mercury thermometer containing nitrogen being used. The freezing point was not so easy to determine, but solidification appeared to begin at about 287°. A mixture containing about 4 mols. of the trichloride, $AuCl_3$, to one of the monochloride, AuCl, melted at 287°, and another mixture, probably of about the same composition, melted at 286° under a pressure of 1·81 atmospheres of chlorine. The presence of the monochloride, therefore, does not much affect the melting point of gold trichloride. After being fused, no metallic gold remains in the mixture, even if it had been originally present.

Specific Gravity of the Chlorides of Gold.—The densities were taken by means of a specific gravity bottle, sulphuric acid being used as the liquid with which to fill the bottle. Neither gold monochloride nor gold trichloride appears to be attacked by sulphuric acid, but the acid was left in contact with a mixture of the two chlorides for 24 hours before being used. In each experiment, some of the chloride was shaken into the bottle, and at the end of the operation it was separated and analysed. Pickering's determinations of the density of sulphuric acid at different temperatures were employed. The gold monochloride was prepared by digesting a fused mixture of the chlorides of gold with ether, and drying the residue at 100°; on analysis, it proved to contain 14·85 per cent. of chlorine, as against 15·2 per cent. according to theory. The weight used was 1·248 grams. The fused mixture of the two chlorides used for the density determination contained 1·9341 grams of gold trichloride and 1·0793 grams of the monochloride. The volatilised trichloride consisted of 0·22 gram of fine, needle-like crystals.

The determinations were made in each case at slightly different temperatures. The results were as follows.

		Mean
Density of AuCl..........	7·35 7 39 7 42	7·4
Density of fused mixture of $AuCl_3$ and AuCl	5·13 5·12 5·09	5 1
Density of fused $AuCl_3$ (calculated)		4 3
Density of volatilised $AuCl_3$		3 9

The last result, being made only at one temperature and on a very small quantity of material, is less trustworthy than the others.

The molecular volumes are therefore—

AuCl .... 32 $AuCl_3$ (fused).. 70

This gives about 20 as the atomic volume of chlorine when in combination with gold, and the agreement with Schröder's theory (*Lehrbuch von allg. Chem.*, 1, 851) is not satisfactory. If, in accordance with this theory, the atomic volume of gold in combination is 10·2 and that of chlorine 15·3, the densities should be

AuCl .... 9·1 $AuCl_3$......... 5 4

On the other hand, if the atom of chlorine is taken as occupying the space of four "steren" instead of only three when in combination with gold, the observed densities and corresponding molecular volumes agree fairly well with the theoretical amounts.

Crystals of Gold Trichloride, $AuCl_3$.—I am kindly allowed by Mr W. J. Pope to add the following communication from him regarding some volatilised crystals of gold trichloride which he examined.

"The crystals mostly consist of small, brilliant prisms, which, when crushed, transmit light of a deep claret-red colour, but show no pleochroism; one or two thin, six-sided plates adhering to the sides of the tube showed an indistinct extinction parallel to one edge of the crystal. The crushed fragments of the massive crystals do not extinguish, even the thinnest remaining bright between crossed nicols; no trace of an interference figure was ever observed, so that the crystals afford an instance of aggregate polarisation. No examination in monochromatic sodium light was possible, as the crystals have a very great absorptive power for light of this colour"

The Royal Mint.

XCI.—*Homonucleal Tri-derivatives of Naphthalene.*

By RAPHAEL MELDOLA, F.R.S., and FREDERICK WILLIAM STREATFEILD, F.I.C.

SINCE the last communication on this subject (Trans., 1892, 765) the investigation has been carried on during all available opportunities, and results have been obtained which appear to us sufficiently interesting to warrant our offering another instalment to the Society.

Dibromonitronaphthalene, $C_{10}H_5Br{\cdot}NO_2{\cdot}Br = 1 : 2 : 4$, *m. p.* 117°.—A considerable quantity of this compound, which was briefly described in the previous communication (p. 769), has been prepared and some of its derivatives studied. Analysis of a specimen purified by crystallisation from alcohol gave the following results.

0·1640 gave 5·95 c.c. moist nitrogen at 14·25° and 756·5 mm. N = 4·23.

0·1520 gave 0·1715 AgBr. Br = 48·01.

$C_{10}H_5Br_2NO_2$ requires Br = 48·33; N = 4·23 per cent.

Dibromo-β-naphthylamine, $C_{10}H_5Br{\cdot}NH_2{\cdot}Br = 1 : 2 : 4$, *m. p.* 106—107°.—The reduction of the nitro-compound is best effected by means of zinc dust and acetic acid in alcoholic solution. The filtered liquid is largely diluted with water, when the dibromonaphthylamine separates out in the form of whitish needles, which must be collected as rapidly as possible and protected from the action of light, as when moist and impure they appear to be susceptible of photochemical oxidation, and become coloured on exposure to the air. The pure compound is, however, quite stable, and when dry consists of white, silky needles melting at 106—107°, and very readily soluble in alcohol, benzene, and all the ordinary organic solvents. A specimen was purified for analysis by crystallisation from dilute alcohol and benzene in succession.

0·1238 gave 5 c.c. moist nitrogen at 17° and 754·3 mm. N = 4·64.

0·0835 gave 0·1040 AgBr. Br = 53·0.

$C_{10}H_5Br_2NH_2$ requires Br = 53·15; N = 4·63 per cent.

The compound is devoid of basic properties. When boiled in glacial acetic acid with a little acetic anhydride, it readily acetylates. The acetyl derivative was purified by crystallisation from acetic acid and alcohol in succession, and was obtained in the form of white needles melting at 220—221°.

0·1567 gave 5·6 c.c. moist nitrogen at 15·5° and 761 mm. N = 4·17

$C_{10}H_5Br_2{\cdot}NH{\cdot}C_2H_3O$ requires N = 4·08 per cent.

Action of Nitrous acid on Dibromo-β-naphthylamine.

An attempt to replace the NH_2-group in the above compound by hydroxyl by the "diazo reaction" led to an unexpected result. The details of the experiment are as follows.

The substance is dissolved in glacial acetic acid, the solution filtered, if necessary, and strong sulphuric acid added till crystals of the sulphate begin to separate out The calculated quantity (or a little excess) of sodium nitrite necessary to diazotise the dibromonaphthylamine is then added in small portions in the solid condition to the well cooled solution, and the mixture allowed to remain for some hours with frequent stirring. On gradually diluting with water, at the same time keeping the liquid cool, a clear solution is obtained, and there is no doubt that at this stage a diazo-salt (sulphate) is present in the solution On raising the latter to the boiling point, little or no nitrogen is evolved, and an ochreous substance gradually separates. The liquid when quite cold deposits a further quantity of a substance crystallising in hair-like ochreous needles. The product, on being collected and washed, proved to be non-phenolic and to contain nitrogen, and was not, therefore, the dibromo-β-naphthol which we were endeavouring to prepare. This fact, combined with the observation above recorded, that practically no nitrogen is evolved on boiling the solution of the diazo-sulphate with water, indicated that the ordinary diazo decomposition had not taken place. The product, on further examination, was found to be resolvable into two portions, one soluble in boiling water, from which it crystallises on cooling in the form of yellowish, filamentous needles. which become brown on exposure to light. The portion insoluble in boiling water consisted of an ochreous compound, very insoluble in all solvents, and most difficult to deal with. It probably contains diazoamido- or an amidoazo-compound, but we have not succeeded as yet in isolating any definite substance from it.

The compound crystallising from water had a decomposing point of about 148—151°, at which temperature it froths up with almost explosive suddenness. It is extremely soluble in alcohol, benzene, glacial acetic acid, and organic solvents generally. A specimen twice crystallised from boiling water was analysed with the following results, from which it appears that the substance is a diazoxide.

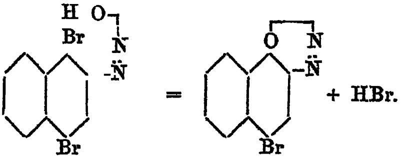
0·1058 gave 9·8 c.c. moist nitrogen at 12° and 763·7 mm. N = 11·03.

0·0971 gave 0·0728 AgBr. Br = 31·90.

0·1424 „ 0·1070 „ „ = 31·97.

$C_{10}H_5BrN_2O$ requires Br = 32·12; N = 11·24 per cent.

The diazoxides, which are anhydrides of ortho- and paradiazophenols, have long been known, and were first prepared by the action of nitrous acid on orthoamidophenols containing acid substituents in the aromatic nucleus (Griess, *Annalen*, 1860, **113**, 212; Schmitt and Glutz, *Ber.*, 1869, **2**, 52; Wagner, *Ber.*, 1874, **7**, 1270; Böhmer, *J. pr. Chem.*, [2], 1881, **24**, 460; Lampert, *ibid.*, 1886, **33**, 375; Kunze, *Ber.*, 1888, **21**, 3333; Conrad and Limpach, *ibid.*, 1978). Diazoxides of the naphthalene series have also been recently obtained by the oxidation of α- and β-diazonaphthalene in alkaline solution with potassium ferricyanide (Bamberger, *Ber.*, 1894, **27**, 679), and by the diazotising of certain dinitro-β-naphthylamines, during which process one of the NO_2-groups is displaced (Gaess and Ammelburg, *Ber.*, 1894, **27**, 2211). The diazoxide, described above, was obtained by us and identified in 1892 as α_4-bromonaphthalene-β_2-diaz-α_1-oxide. Its formation is best explained by the following scheme, in which the free diazo-compound is represented as taking part in the process of inner condensation with the elimination of bromine. The isodiazo-form is inadmissible in this case, as the transformation occurs in the presence of excess of strong sulphuric acid.



This view of the formation of the diazoxide is confirmed by the presence of bromohydric acid in the mother liquor after the crystalline deposit has been removed by filtration. The compound was further characterised by bromination and reduction. When a solution of bromine in glacial acetic acid is added in excess to a solution of the diazoxide in the same solvent, nitrogen is evolved, and on allowing to stand for some hours a crystalline deposit gradually forms. After repeated crystallisation from glacial acetic acid, the product was obtained pure, and proved to be dibromo-α-naphthaquinone, m. p. 216°.*

0·1648 gave 0·1963 AgBr. Br. = 50·68.

$C_{10}H_4Br_2O_2$ requires Br = 50·63 per cent.

The characteristic anilide crystallising in red scales melting at 190° was also prepared. The formation of dibromo-α-naphthaquinone from the diazoxide by the action of bromine, is certainly a point of some interest, because the α_4-Br atom must be displaced under the influence of the same element exerted as an oxidising agent. In fact, the facility with which α-substituents can be removed from the naphthalene ring, especially when the neighbouring β-position is also substituted, is quite remarkable, as is seen by the displacement of the bromine-atom in the formation of the diazoxide, and even more strikingly in the displacement of the NO_2-group in the method of Gaess and Ammelburg above referred to. An illustration of the same point is furnished by Liebermann and Scheiding's original method of preparing β-naphthylamine, now of historical interest only, in which nitro-2-bromo-4-naphthalene loses its bromine on reduction with tin and hydrochloric acid (*Annalen*, 1876, **183**, 253).

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* Trans., 1890, 809 (Meldola and Hughes). The corresponding dihydro-derivative obtained by reduction gives a diacetyl (m. p. 238°), and not a monacetyl derivative on acetylation with sodium acetate and acetic anhydride as stated in the paper referred to (p. 810). A repetition of the analysis has led us to this conclusion, which is quite in harmony with the non-phenolic character of the compound.

From considerations such as the foregoing, it might have been expected that our bromodiazoxide would lose its bromine-atom on energetic reduction, and thus give 2 : 1-amidonaphthol. This conclusion has been borne out by experiment. Some of the compound was reduced by boiling in alcoholic solution with tin and hydrochloric acid; the solution was filtered, the alcohol evaporated off, and the amidonaphthol precipitated as hydrochloride by adding excess of strong hydrochloric acid. The white precipitate was collected, redissolved in water, and re-precipitated by hydrochloric acid, the operation being repeated till the compound was practically free from tin salts.

The substance had all the properties of the expected amidonaphthol. When basified by ammonia and exposed to the air, the violet colour of naphthaquinoneimide, $C_{10}H_6{<}\genfrac{}{}{0pt}{}{O}{NH}$, made its appearance. A solution of the hydrochloride, when warmed with ferric chloride, gradually deposited orange crystals of α-dinaphthyldiquinone, the latter being identified by its characteristic basic tetranilide; m. p. 248—250° (Korn, *Ber.*, 1884, **17**, 3022).

Chlorobromo-β-naphthylamine, $C_{10}H_5{\cdot}Cl{\cdot}NH_2{\cdot}Br$ = 1 : 2 : 4, *m. p.* 102—103°.—In the previous paper (Trans., 1892, 768) this compound was only provisionally described. We have since prepared it in larger quantities, and by repeated crystallisation, first from dilute, and finally from absolute alcohol, we have obtained it in the form of white, silky needles melting at 102—103°. It is devoid of basic properties, like the corresponding dibromo-β-naphthylamine. The acetyl derivative has the melting point (218°) already assigned. As the nitrogen only had been determined in the former preparation, we give the result of determining the halogens:—

0·1030 gave 0·1329 AgCl + AgBr. Cl + Br = 44·94.

$C_{10}H_5ClBr{\cdot}NH_2$ requires Cl + Br = 45·03 per cent.

In order to further characterise the substance, the benzoyl derivative was prepared by agitating the base suspended in water with benzoyl chloride, and adding caustic soda solution, drop by drop, till the transformation into the benzoyl derivative was complete. After crystallisation from alcohol the compound consists of beautiful silvery, flattened needles.

0·1264 gave 4·3 c.c. moist nitrogen at 14° and 757·2 mm. N = 3·98.

$C_{10}H_5ClBr{\cdot}NH{\cdot}C_7H_5O$ requires N = 3·88 per cent.

The pure compound has a melting point of 185—186°.

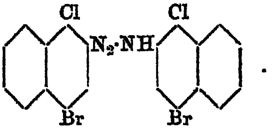
Action of Nitrous acid on Chlorobromo-β-Naphthylamine.

The products in this case vary according to the conditions of the experiment. When the base is dissolved in alcohol and sodium nitrite added to the cold solution, an ochreous crystalline substance separates out, and a further crop of the same compound is obtained by diluting the filtrate with water. This substance proved to be a diazoamido-compound. It was purified by crystallisation from boiling toluene, and then formed yellowish needles having a decomposing point of about 205—210°.

0·1452 gave 10·25 c.c. moist nitrogen at 21·5° and 750 mm. N = 7·91.
0·1544 „ 10·75 c.c. „ 18·5° „ 758·8 „ N = 8·02.
0·1392 „ 0·1762 AgCl + AgBr. Cl + Br = 44·10.

The formula requires N = 8·01 and Cl + Br = 44·08 per cent.

The diazoamido-compound has the following constitution:—



It is more stable than the majority of the diazoamido-compounds, but it is now well known that the accumulation of acid radicles in the molecules increases the stability to a remarkable extent (Zettel, *Ber.*, 1893, **26**, 2471; and Herschmann, *Ber.*, 1894, **27**, 767). The compound is decomposed on boiling with dilute sulphuric acid (about equal volumes of strong acid and water), the products being nitrogen, chlorobromonaphthylamine, and a resinous substance which could not be crystallised.

When chlorobromo-β-naphthylamine is diazotised in glacial acetic acid in the presence of strong sulphuric acid, the decomposition follows the same course as in the case of dibromo-β-naphthylamine under similar conditions, the diazoxide, $C_{10}H_5Br{<}\overset{O}{\underset{N_2}{|}}$ (decomposing point, 148—151°) being formed. In glacial acetic acid only, there is produced, by the action of sodium nitrite, a mixture of diazoamide and diazoxide. Under no conditions has it been found possible to replace the NH_2-group by hydroxyl by the diazo-reaction.

Homonucleal Tri-derivatives containing Iodine.

In a paper published by one of us 10 years ago (Trans., 1885, **47**, 523), a nitroiodoacetnaphthalide, and the corresponding nitroiodonaphthol, were described. These compounds were obtained by a very laborious method, and only in small quantity, owing to the bad yield. We have now to describe a more direct method of preparing these derivatives, which has enabled us to obtain them in considerable quantity, and to characterise them more fully than was possible at the time of the earlier work.

α-Acetnaphthalide is best converted into the iodo-derivative by the action of the calculated quantity of iodine monochloride, both substances being dissolved in glacial acetic acid. On allowing to stand for some days, iod-α-acetnaphthalide separates out as a white, crystalline pulp; the separation of this compound takes place more rapidly if the solution is slightly warmed. The substance has the properties described in the former paper; the melting point was found to be 197° (196° in a previous paper). As no analysis was formerly given, we add the following.

0·2299 gave 8·9 c.c. moist nitrogen at 16° and 758 1 mm. N = 4·49.
$C_{10}H_6I{\cdot}NH{\cdot}C_2H_3O$ requires N = 4·51 per cent.

Nitroiodo-α-acetonaphthalide, $C_{10}H_5{\cdot}NO_2{\cdot}I{\cdot}NH{\cdot}C_2H_3O$ = 2 : 4 : 1. —This substance is best prepared by covering pure iod-α-acetnaphthalide with glacial acetic acid, and then adding about double the calculated quantity of fuming nitric acid, of sp. gr. 1·5, diluted with an equal volume of acetic acid. The solution gets warm enough on stirring to dissolve up the iodo-derivative, and the nitroiodo-compound separates out in a crystalline form on allowing the solution to stand. It is better not to apply heat as described in the earlier method, since there is a tendency under these circumstances for the iodine to become partly replaced by the NO_2-group, and the resulting product is thus liable to be rendered impure by admixture with dinitro-α-acetnaphthalide, which is easily formed from the nitroiodo-derivative by the action of excess of nitric acid on the latter, especially when the nitric acid solution is heated.

Pure nitroiodo-α-acetnaphthalide forms pale, straw-coloured needles, having a melting point of 242°, after repeated crystallisation from glacial acetic acid (melting point of impure substance formerly given as about 236°).

0·0891 gave 6·1 c.c. moist nitrogen at 12·5° and 756·7 mm. N = 8·06.
0·0815 „ 0·0538 AgI. I = 35·61.
The formula requires N = 7·88 ; I = 35·58 per cent.

The difficulty of hydrolysing this compound without at the same time removing iodine, as mentioned in the former paper, has been amply confirmed, and we have been unable to obtain the nitroiodo-α-naphthylamine, or the corresponding metanitroiodonaphthalene.

Nitroiodo-α-naphthol, $C_{10}H_5 \cdot NO_2 \cdot I \cdot OH$ = 2 : 4 : 1.—The preparation and properties of this compound have been described in the paper of 1885 (*loc. cit.*, p. 524). We find that by repeated crystallisation from glacial acetic acid, the melting point becomes 150°, but the compound begins to shrink before it melts at 147—148°.

0·1083 gave 4·35 c.c. moist nitrogen at 21° and 767·6 mm. N = 4·61·
The formula requires N = 4·47 per cent.

In order to further characterise this compound, the potassium salt was prepared and analysed. It consisted of orange needles, which were crystallised from boiling water.

0·2404 dried at 100—110° till constant in weight lost 0·0124 = H_2O, 5·07.
0·2280 gave 0·0550 K_2SO_4. K = 10·81.
The formula $C_{10}H_5 \cdot NO_2 \cdot I \cdot OK,H_2O$ requires H_2O = 4·85 and K = 11·05 per cent.

The ethyl ether, $C_{10}H_5 \cdot NO_2 \cdot I \cdot OC_2H_5$, was also prepared by treating the silver salt (a brick-red powder) with ethyl iodide. It forms pale yellow, flattened needles or scales when crystallised from alcohol, in which it is extremely soluble. The melting point is 104—105°.

In conclusion, we may add that iodine chloride readily forms an iodine derivative of β-acetnaphthalide, which is now under investigation. The foregoing research has been taken part in by several of our students, and we desire to express our thanks more particularly to Messrs. F. B. Burls, H. W. Younger, and E. R. Andrews.

Finsbury Technical College.

XCII.—*The Ethereal Salts of the Optically Active Lactic, Chloropropionic and Bromopropionic Acids.*

By J. Wallace Walker, M.A., Exhibition Science Scholar, St. Andrew's University.

During the past few years the ethereal salts of a number of optically active acids have been prepared and examined, with the object of discovering some numerical relationship between their degree of optical activity and the masses of the different radicles attached to the asymmetric carbon atoms. The first approach to a generalisation was proposed independently by Crum-Brown and by Guye. Crum-Brown (*Proc. Roy. Soc.*, Edin., **17**, 181) showed that in the case of the ethereal tartrates and their acetyl derivatives certain changes in the mass and constitution of the radicles produce definite changes, both in the magnitude and sign of the rotation. He also put forward the opinion that it may be possible to determine for each atom and radicle a function κ, which will express the amount of influence that the atom or radicle will have on the rotation of any asymmetric system into which it may be introduced; and he indicated how some idea may be gained as to the relative values of the functions of a number of radicles.

Guye (*Compt. rend.*, 1893, **116**, 1451) takes as his starting point the assumption that the geometric form of the molecule of an active substance may vary so little from that of a regular tetrahedron that the difference may be neglected. Owing to the difference in mass of the radicles, however, the centre of gravity of the molecule must lie outside of all the six planes of symmetry of the regular tetrahedron, and he believes that the asymmetry of the substance, on which its rotatory power depends, could be calculated from the amount of displacement of the centre of gravity from these six planes of symmetry. Since, however, it is impossible to determine these distances, and as they must depend to a large extent on the masses of the radicles, he uses the masses alone to calculate the direction of change in rotation of an asymmetric system by the gradual increase in mass of one of its groups. That this method cannot give general results has been clearly shown, for many active substances are known in which two of the groups are different in constitution but equal in mass, and, according to Guye, such compounds should be inactive. It also very seldom occurs that the propylic and isopropylic, butylic and isobutylic salts of the same acid have an equal rotation. Again, if, in an asymmetric system, C, *a*, *b*, *c*, *d*, where the masses of the radicles attached to the carbon atom increase from *a* to *d*, *d* be substituted by a radicle whose mass is greater than that of *c*, Guye's method of calculation from the masses alone implies first that the sign of the rotation should remain unchanged, and second that the rotation should increase with increase of mass. The first of these conclusions he substantiated by the preparation of more than 40 derivatives of active amylic alcohol, nearly all of which preserved the same sign. As regards the second, however, Walden has shown (*Zeit. physikal. Chem.*, 1895, **15**, 638) by the examination of a large number of derivatives of the same substance, that few of them are in accordance with it. One of Walden's most striking observations was the great difference between the rotations of amylic fumarate and maleate. This would seem to show that the influence of a radicle on the rotation may depend as much on the nature of the radicle as on its mass, and the observations to be described in this paper lead to the same conclusion. Guye himself admits (*loc. cit.*) that his method of calculation can apply at best to simple compounds where the amount of dissimilarity between the groups is not sufficient to lead us to expect much distortion in the figure of the molecule; but it may be doubted if even in the ethereal glycerates, which he cites as a case in which there is very close agreement between the position of the maximum point calculated from his formula and that observed, there may not be sufficient attraction between H and OH to cause considerable distortion. Certainly, as will be seen later, the rotations of the ethereal lactates, which are at least as simple bodies as the glycerates, show no agreement with the numbers calculated. It seems to me, therefore, that the method most likely to lead to a generalisation is to examine the ethereal salts of a sufficient number of closely allied simple acids, and so to determine whether there is such a thing as a constant rotation equivalent for each radicle or not. For this purpose I have prepared some ethereal salts of lactic, chloropropionic, and bromopropionic acids.

It is, of course, probable, as Nernst points out, that an atom or group has no constant function, κ, or *rotation equivalent*, but that its influence on the rotation depends on the atoms or groups already present in the body into which it is introduced. It is scarcely likely that when bromine, for example, is introduced into various compounds, the position it takes up is always at the same distance from the carbon atom; and this difference of distance might affect the rotation of the new substances in different degrees, unless it were counterbalanced by some such factor as difference of velocity of vibration.

While this investigation has been in progress, two papers have appeared dealing with parts of the same subject. Frankland and Henderson (*Proc. Chem. Soc.*, 1895, **11**, 54) have prepared the methylic and ethylic lactates from lactic acid, presumably by the hydrochloric acid method, and they attempt to reconcile the observed results with Guye's theory. But as the rotations observed by them are far below the actual values, no reliable conclusions can be drawn from them. The authors do not allude in the paper to the fact that Klimenko (*J. Russ. Chem. Soc.*, **12**, 30) had already prepared lævo-ethylic lactate, and found for it the specific rotation −14·19°, a value which agrees very closely with my own observation, but is far in excess of that quoted by them, viz., −8·6°.

Walden (*Ber.*, 1895, **28**, 1293), in a research on active chloro- and bromo-ethereal salts, has prepared the methylic and ethylic chloropropionates and ethylic bromopropionate. I am not yet in a position to state the actual values of the rotations of the chloro-salts, but those given by Walden are too low, doubtless, as will appear later, because his preparations were mixed with a substance of opposite activity. In the case of the bromo-salt, he seems to be aware that the value he has found for $[\alpha]_D$ is too small, and this is, indeed, the case. Instead of its specific rotation being −7°, it is 31°. The source of this large error is probably to be found in the fact that it was prepared from an ethereal lactate which had been made by the hydrochloric acid method, but as he does not give the rotation of the ethylic lactate, it is impossible to say with certainty. It is also noteworthy that the author gives no analyses to show whether the preparations he has examined were the supposed substances or not.

EXPERIMENTAL PART.

The active lactic acid, from which these ethereal salts were made, was prepared as described in a recent paper (Purdie and Walker, Trans., 1895, **67**, 616).

Ethereal Lactates.

The ethereal lactates were prepared by the action of their respective iodides on the silver salt, which had been carefully dried at 100°.

Lævo-methylic Lactate.—Forty-five grams of the dry silver salt of *d*-lactic acid were slowly added to 66 grams of methylic iodide. The reaction was very vigorous, but the silver salt seemed to turn pasty and get coated with silver iodide. The mixture was finally heated a short time on the water bath. When distilled under a pressure of 200 mm., 12 grams passed over at 105·5—106°. Analysis showed that this was pure methylic lactate.

0·2463 gave 0·4174 CO_2 and 0·1700 H_2O. C = 46·22; H = 7·67.
$C_4H_8O_3$ requires C = 46·15; H = 7·69 per cent.

A determination of its specific rotation gave the following results.

$\alpha = -12{\cdot}21^\circ$; $l = 100$ mm.; $d_4^{19} = 1{\cdot}100$; hence $[\alpha]_D = -11{\cdot}1^\circ$.

Le Bel prepared this salt by allowing a mixture of lactic acid and methylic alcohol to stand over quicklime, and found for it a rotation of $-8{\cdot}5^\circ$ in a 100 mm. tube. As has been already mentioned, Frankland and Henderson find for the same substance a specific rotation still lower, viz., $[\alpha]_D = -6{\cdot}8^\circ$. It seems possible, therefore, that the rotation of this salt is diminished both by distillation at the ordinary pressure and by heating with hydrochloric acid.

Dextro-ethylic Lactate.—Ninety grams of the silver salt of *l*-lactic acid were treated in the same manner as in last experiment with 150 grams of ethylic iodide. The general appearance of the reaction was the same, and, on fractionating under diminished pressure, 29 grams were obtained boiling constantly at 67—64°, under a pressure of 25—22 mm. A combustion showed the purity of the substance.

0·234 gave 0·4334 CO_2 and 0·1791 H_2O. C = 50·51; H = 8·50.

$C_5H_{10}O_3$ requires C = 50·85; H = 8·47 per cent.

Its specific rotation was found to agree very closely with the value given by Klimenko (*loc. cit.*), viz., $+14{\cdot}19^\circ$.

$\alpha = +14{\cdot}96^\circ$; $l = 100$ mm.; $d_4^{19} = 1{\cdot}030$; hence $[\alpha]_D = +14{\cdot}52^\circ$.

Frankland and Henderson find for the same salt a specific rotation of $+8{\cdot}6^\circ$.

To show the necessity of purifying the salt completely from other substances, the following observations of its specific rotation taken in chloroform and benzene may be cited.

In chloroform—

I. $c = 6{\cdot}1715$; $\alpha = +1{\cdot}33^\circ$; $l = 400$; hence $[\alpha]_D = +5{\cdot}39^\circ$.
II. $c = 1{\cdot}2343$; $\alpha = +0{\cdot}27^\circ$; $l = 400$; hence $[\alpha]_D = +5{\cdot}47^\circ$.

In benzene—

I. $c = 5{\cdot}941$; $\alpha = +1{\cdot}42^\circ$; $l = 200$; hence $[\alpha]_D = +10{\cdot}61^\circ$.
II. $c = 1{\cdot}188$; $\alpha = +1{\cdot}04^\circ$; $l = 400$; hence $[\alpha]_D = +21{\cdot}89^\circ$.

Freundler (*Compt. rend.*, 1893, **117**, 556) has made an extensive series of experiments on the influence of various solvents on the rotations of ethereal derivatives of tartaric acid. He found that the effect of the two solvents used above was almost the same, and that they caused the rotation of the salts to become either very small or of opposite sign. In the four observations given above, it is very remarkable that, whilst the specific rotation of the salt in chloroform solution is very small, and apparently unchanged on dilution, in benzene it is only slightly diminished, and increases very much in more dilute solution. These results are not due to decomposition of the salt into acid and alcohol, as Freundler has observed in the case of the tartrates, for all the solutions were found to give a perfectly neutral reaction.

Lævo-propylic Lactate.—Twenty-five grams of the silver salt of *d*-lactic acid were added, as before, to 38 grams of propylic iodide. After repeated fractional distillation, there remained 6 grams of a liquid boiling at 122—123° under a pressure of 150 mm. Analysis showed that it was pure propylic lactate.

0·1867 gave 0·3724 CO_2 and 0·1520 H_2O. C = 54·40; H = 9·05
$C_6H_{12}O_3$ requires C = 54·55; H = 9·09 per cent.

A determination of its specific rotation gave the following value.

$\alpha = -17\cdot13°$; $l = 100$ mm.; $d_4^{10} = 1\cdot004$; hence $[\alpha]_D = -17\cdot06°$.

Ethereal Chloropropionates.

Dextro-ethylic Chloropropionate.—It has been shown by Würtz (*Annalen*, 1858, **107**, 192) and Bruhl (*Ber.*, 1876, **9**, 35) that the inactive salt can be readily obtained by the action of phosphorus pentachloride on *i*-calcium lactate and *i*-lactic acid, and subsequent treatment with alcohol. It seemed to me quite probable that the corresponding active substance might be obtained by using the zinc salt, thus avoiding the preparation of the calcium salt. Accordingly 62 grams of lævo-zinc lactate were added to 135 grams of phosphorus pentachloride in a retort, but there was instant charring, and only a small quantity of a distillate was obtained, which was added to some alcohol. On pouring this alcoholic liquid into a relatively large volume of water, only a few drops of an oil separated. So the method was abandoned as entirely unsuitable.

Sixty grams of the calcium salt dried at 100° were heated on an oil bath, 20 grams at a time with 50 grams of phosphorus pentachloride, and the united distillates were added to ethylic alcohol. On pouring this solution into much water, 14 grams of a heavy oil separated which was washed with solution of sodium carbonate, dried and distilled. After being twice fractionated, it gave 5 grams, boiling at 47° under a pressure of 17—20 mm. Analysis showed that it was nearly pure ethylic chloropropionate.

0·1899 gave 0·3035 CO_2 and 0·1107 H_2O. C = 43·59; H = 6·48.
$C_5H_9O_2Cl$ requires C = 43·96; H = 6·59 per cent.

Its specific rotation was found to have a much higher value than that assigned to it by Walden (*loc. cit.*), viz., 12·86°.

$\alpha = +21\cdot21°$; $l = 100$ mm.; $d_4^{11\cdot5} = 1\cdot087$; hence $[\alpha]_D = +19\cdot51°$

As the yield of active salt was still very unsatisfactory, Brühl's method was next adopted, *i.e.*, the action of phosphorus pentachloride on free lactic acid.

Thirty-three grams of *d*-lactic acid syrup were slowly added to 164 grams of phosphorus pentachloride in a retort fitted with a reflux condenser. The reaction was very violent, but it was only on warming that the pentachloride entirely disappeared. The mixture was gently heated for half an hour, and on cooling 200 grams of ethylic alcohol were slowly run into it. After standing for 24 hours this solution was poured into much water. Thirty-eight grams of a heavy oil separated which was washed with sodium carbonate solution and dried with calcium chloride. After repeated fractional distillation under diminished pressure, 14·5 grams were obtained boiling at 46·5—47° under 17—20 mm. pressure. A considerable quantity of a higher boiling liquid is also produced in the reaction. It has a rotation in the opposite sense to that of the chloropropionate, but it has not yet been purified by distillation. The low rotation found by Walden for this salt may possibly be due in part to the presence of this impurity. The specific rotation of the salt prepared from lactic acid was found to agree very closely with that of the salt prepared from the calcium salt.

$\alpha = + 21·78°$; $l = 100$ mm.; $d^{15}_{4} = 1·096$; hence $[\alpha]_D = + 19·88°$.

Lævo-methylic Chloropropionate.—Fifty grams of *l*-lactic acid syrup were treated in a similar way with 275 grams of phosphorus pentachloride, and on cooling 230 grams of pure methylic alcohol were slowly added to the mixture. After 20 hours, it was poured into much water, but only 20 grams of oil separated. The solution was accordingly neutralised and extracted with ether. After repeated fractional distillation, 14 grams were obtained boiling at 78·5—80° under 120 mm. pressure.

Analysis showed it to be nearly pure methylic chloropropionate.

0·3026 gave 0·4288 CO_2 and 0·1527 H_2O. C = 38·65; H = 5·61

$C_4H_7O_2Cl$ requires C = 39·19; H = 5·71 per cent.

It was found to give a rotation of —59·5° in the 200 mm. tube at the ordinary temperature, and an exact determination of the specific rotation gave the following value :—

$\alpha = - 31·07°$; $l = 100$ mm.; $d^{1}_{4} = 1·158$; hence $[\alpha]_D = - 26·83°$.

The value found by Walden for this salt is 19·01°.

Dextro-propylic Chloropropionate.—Thirty grams of *l*-lactic acid syrup were treated in a similar manner with 150 grams of phosphorus pentachloride; 225 grams of propylic alcohol were then slowly added to the mixture, which was heated for a short time, and then allowed to stand 12 hours On pouring this solution into water, much oil separated which had a *lævo*-rotation of between 4° and 5° in the 100-mm. tube. Sodium carbonate dissolved a considerable quantity of it, and from the alkaline solution an oil was again precipitated by addition of acid. This acid oil was strongly *lævo*-rotatory. The oil remaining undissolved by sodium carbonate was dried with calcium chloride and distilled under reduced pressure. After repeated fractional distillation and loss of much substance, the salt was obtained boiling at 57° under a pressure of 12 mm. The yield amounted only to 6 grams.

Analysis showed that it was approximately pure propylic chloropropionate.

0·2495 gave 0·4308 CO_2 and 0·1611 H_2O. C = 47·09 ; H = 7·18.
$C_6H_{11}O_2Cl$ requires C = 47 84; H = 7 31 per cent.

A determination of the specific rotation gave the following result:—

$\alpha = +11{\cdot}71°$; $l = 100$ mm,; $d^{0}_{4} = 1{\cdot}065$; hence $[\alpha]_D = +11{\cdot}0°$.

Ethereal Bromopropionates.

The bromo-salts were also prepared at first by the action of phosphorus pentabromide on lactic acid; but decomposition seemed to set in much more readily than with pentachloride, and it was found in attempting to prepare the propylic salt, that by far the greater part of the product was a high-boiling substance of opposite activity to the bromo-salts. It seemed therefore quite probable that, even in the methylic and ethylic salts, where a high degree of optical activity had been observed, there might be a considerable amount of racemoid substance present, produced by heating the comparatively unstable bromopropionate in the presence of such energetic reagents as strong hydrobromic acid and phosphorus oxybromide. The salts were accordingly prepared by acting with phosphorus pentabromide upon ethereal lactates dissolved in chloroform, by which means heating was avoided and the reaction effected in a very short time, so that transformation into the racemoid form was almost impossible. The result of the experiments with lactic acid are given below, as well as those with ethereal lactates.

Dextro-methylic Bromopropionate.—This substance was prepared from *d*-lactic acid in the same way as the corresponding chloro-salt but as the temperature was allowed to rise too high, some decomposition took place and the quantity of material obtained by fractional distillation was insufficient for complete purification. Its boiling point was 62—63° under a pressure of 30 mm, and the rotation observed in the 100-mm. tube was +25°.

It was afterwards prepared from lævo-methylic lactate. Twelve grams of this salt dissolved in 30 c.c. of chloroform were slowly added to 50 grams of phosphorus pentabromide. The reaction scarcely started till the flask was placed in warm water. After all the pentabromide had gone into solution, the liquid was cooled and water was slowly added to it; the aqueous solution was neutralised with sodium carbonate and extracted with ether. This ethereal solution of the salt was dried with sodium sulphate, and after evaporation of the ether, the residue was distilled under diminished pressure; 4·5 grams passed over at 96—93° under a pressure of 135—120 mm. This fraction was evidently not quite pure, but as it was too small for further purification, it was analysed and examined in the polarimeter.

0·3963 gave 0·4008 CO_2 and 0·1432 H_2O. C = 27·58; H = 4·01.
$C_4H_7O_2Br$ requires C = 28·74; H = 4·19 per cent.

A determination of its specific rotation showed how very impure was the substance prepared directly from the acid.

$\alpha = + 63{\cdot}20^\circ$; $l = 100$ mm.; $d_4^{17} = 1{\cdot}482$; hence $[\alpha]_D = + 42{\cdot}65^\circ$.

Lævo-ethylic bromopropionate.—This salt was also prepared at first from *l*-lactic acid, but, in spite of every precaution being taken to keep the temperature as low as possible, it was afterwards found that about 50 per cent. of the salt had been rendered inactive. Its boiling point was at 63° under 20 mm. pressure and its specific rotation as follows:—

$\alpha = - 20{\cdot}08^\circ$; $l = 100$ mm.; $d_4^{6} = 1{\cdot}410$; hence $[\alpha]_D = - 14{\cdot}24^\circ$.

A quantity of the dextro-salt prepared in the same manner had an almost identical rotation, and an analysis by combustion showed that it was nearly pure ethylic bromopropionate.

0·394 gave 0·4745 CO_2 and 0·174 H_2O. C = 32·84; H = 4·91.
$C_5H_9O_2Br$ requires C = 33·15; H = 4·97 per cent.

The lævo-salt was also prepared from dextro-ethylic lactate. Eighteen grams of this salt dissolved in 40 c.c. of chloroform were slowly added to 66 grams of phosphorus pentabromide. It required slight warming to dissolve the whole of the pentabromide. The product was treated in the same way as in the preparation of the methylic salt, and when subjected to fractional distillation yielded 9·5 grams boiling at 87° under a pressure of 59—56 mm. A combustion showed that it was almost pure.

0·2591 gave 0·3171 CO_2 and 0·1187 H_2O. C = 33·38; H = 5·09.

A determination of its specific rotation gave the following results:

$\alpha = - 43{\cdot}59^\circ$; $l = 100$ mm.; $d_4^{10} = 1{\cdot}386$; hence $[\alpha]_D = - 31{\cdot}45^\circ$.

The value found by Walden for the specific rotation of this salt was −7·18°.

Lævo-propylic Bromopropionate.—An attempt was made to prepare the propylic salt also from lactic acid, but it resulted entirely in the formation of high boiling substances of opposite activity to the bromopropionates. It was accordingly prepared from *d*-propylic lactate, in the manner above described for the methylic and ethylic salts. From 16 grams of propylic lactate, 7 grams of the new bromo-salt were obtained boiling at 94° under a pressure of 50 mm. It was re-distilled and gave 5 grams boiling at 86—84° under 32—28 mm. pressure. An analysis showed that it was nearly pure.

0·3348 gave 0·4569 CO_2 and 0·1711 H_2O. C = 37·22; H = 5·68.
$C_6H_{11}O_2Br$ requires C = 36·92; H = 5·64 per cent.

A determination of its specific rotation gave the following value:—

$\alpha = -28{\cdot}90°$; $l = 100$ mm.; $d_4^{14} = 1{\cdot}315$; hence $[\alpha]_D = -21{\cdot}98°$.

The results obtained for these bromo-salts show that we can be certain of obtaining the halogen derivatives of the active acids quite free from admixture with the racemoid form only by means of the ethereal salts of the hydroxy-acids. The values given above for the specific rotations of the chloro-salts cannot therefore be regarded with certainty as correct, still the fact that ethylic chloropropionate was obtained by two different methods with the same degree of activity would seem to indicate that it at least is pure, and that the chloro-salts are much less liable than the bromo-salts to lose their activity when prepared directly from the hydroxy-acids.

The results obtained for these nine ethereal salts are arranged below in tabular form, and in order that their relationship to each other may be quite evident, I have regarded them as all derived from *dextro*-lactic acid.

	$[\alpha]_D$	$\frac{M[\alpha]_D}{100}$.	Difference for CH_2	P × 10^6.
Methylic lactate	−11·10°	−11·54°	5·50°	79
Ethylic "	−14·52	−17·13	5 39	74
Propylic "	−17·06	−22·52		65
Methylic chloropropionate..	+26·83	+32·87	5·73	326
Ethylic " ...	+19·88	+27·14	10·58	416
Propylic " ...	+11·00	+16·56		447
Methylic bromopropionate..	+42·65	+71·33	11·31	—
Ethylic " ..	+31·45	+57·02	14·16	—
Propylic " ..	+21·98	+42 86		—

The first general observation to be made regarding the above numbers is that whilst the ethereal lactates rotate in the opposite sense to the lactic acid from which they are produced, the chloro- and bromopropionates rotate in the same sense, that is to say the introduction of halogen in the place of hydroxyl in the ethereal salts changes the sign of rotation. Again, in the lactates, if the product of asymmetry be calculated from Guye's formula, the maximum ought to occur at the methylic salt, whereas there is a continued and large increase in molecular rotation as far at least as the propylic salt, and possibly further. This method of calculation of the product of asymmetry fails equally to harmonise with the results observed in the ethereal chloropropionates, for in this series a maximum should occur at the propylic, whilst as a matter of fact the rotation decreases regularly from the methylic to the propylic salt. In the bromo-salts, the assumption that the masses alone of the radicles can be used as a measure of the amount of asymmetry is disproved entirely, because whilst Br (= 80) is the heaviest of the four groups in the methylic and ethylic salts, in the propylic salt the mass of $COOC_3H_7$ (= 87) is greater than that of Br, consequently there ought to be a change in sign of rotation in passing from the ethylic to the propylic salt—a conclusion not in the least borne out by observation. Again, if mass is the chief factor determining the direction of rotation, there is no reason why there should be a change of sign from the ethereal lactates to the chloropropionates, as there is no change in the order of mass of the radicles. Such a change, however, does occur in passing from methylic chloropropionate, where $COOCH_3$ (= 59) is greater than Cl (= 35·5), to methylic bromopropionate, and yet there is no change of sign in the rotation. On the contrary the rotation of the bromo-salt far exceeds that of the chloro-salt.

If we consider the molecular rotations of the ethereal lactates we find that there is a constant increase of 5·5° for the addition of CH_2 to the carboxyl-group. In other words, if a curve be plotted for this series in which the abscissæ represent the molecular weights and the ordinates the molecular rotations, the three points are found to lie on a straight line. The same is true of the ethereal bromopropionates, the difference between the methylic and the ethylic being 14·3°, that between the ethylic and the propylic salts, 14·2°. A constant difference of rotatory power does not appear between the members of the chloropropionic series, but this is also the one series where we have reason to suspect that some of the rotations observed may be lower than the real values. The same relationship appears in the series of ethereal glycerates prepared by Frankland and MacGregor (Trans., 1893, 63, 1415), where there is an almost constant difference of 6·5° for the same three members. Now, even although the maximum point of a series calculated from the product of asymmetry does not agree with observation, it might be expected that the values obtained from Guye's equation would show some indication of this regular increase, but they do not do so.

The whole relationship of this group seems to me to point to the conclusion that, as Crum-Brown at first supposed, κ must be "a function of the composition and constitution of the radicle, not necessarily proportional to the mass and the distance of the centre of gravity from the centre of the tetrahedron;" and that the equation to be used for finding the values of the κ's of the radicles will contain the product of the differences of the κ's, not of the masses. If it contains this alone, then from these nine ethereal salts we shall have nine equations and only eight unknowns, so that they ought to be soluble. I wish, however, to delay consideration of this point until I have prepared the chloropropionates from the ethereal lactates also. When the values of κ for H, CH_3, OH, and $COOCH_3$ are determined, there will be plenty of material in the ethereal salts of valeric, glyceric, and malic acids for testing whether these values are constant or not.

Although we are not yet in a position to calculate the absolute values of κ, this much can be said, that the κ of hydroxyl has a very different value from the κ of the halogens. Besides in the ethereal lactates, chloropropionates, and bromopropionates, this change of sign appears in a large number of compounds already prepared, in some of which there is a change in the order of magnitude, in others no change. For example, *l*-amylic alcohol, in which the order of magnitude of the radicles is H. CH_3, C_2H_5, CH_2OH, undergoes no change in the order of mass when hydroxyl is replaced by the halogens, yet all the halogen derivatives are of opposite rotation to the alcohol. Again, secondary *l*-amylic alcohol, in which the order is H, CH_3, OH, C_3H_7, undergoes no change in the order of mass by the substitution of chlorine for hydroxyl, though it does so if iodine be used instead of chlorine, yet both chloride and iodide are *dextro*-rotatory. The same influence appears very strongly in all the chloro- and bromo-salts prepared lately by Walden (*loc. cit.*), though it is not noted by him. In chlorosuccinic acid, its di-methylic and diethylic salts, as well as in ethylic chloromalate, there is no change in the order of mass of their radicles from that of the hydroxy-acids and ethereal salts from which they are produced, yet they all possess a rotation in the opposite sense to that of their corresponding hydroxy-compound. The powerful effect of the halogens on the rotation is also very marked in the derivatives of mandelic acid. In phenylchloracetic acid and its ethylic salt, the order of mass of the groups is the same as in mandelic acid, from which they are prepared, whilst in phenylbromacetic acid and in its ethylic salt, as well as in the propylic salt of phenylchloracetic acid, there is a change in the order: yet all these rotate in the opposite sense to the mandelic acid from which they are made. It seems quite certain, therefore, that this change in the sign of rotation in passing from the salts of the hydroxy-acids to their corresponding halogen derivatives is due to the great difference in value of the function of hydroxyl from that of the halogens. The values given above for the rotations of the chloro- and bromopropionates, taken along with those given by other investigators for other active chloro- and bromo-compounds, seem to me to warrant one other conclusion, viz., that since almost all bromo-derivatives are found to have a greater rotation than the corresponding chloro-derivatives, the rotation equivalent of bromine must exceed that of chlorine. But whether the rotation equivalents of analogous radicles are directly proportional to their masses or not is a problem still awaiting solution.

In conclusion, I wish to express my thanks to Dr. Purdie, in whose laboratory this investigation was carried out, for the interest which he has taken in the whole progress of the research.

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XCIII.—*Some New Azo-compounds.**

By Charles Mills, Assoc. C.G.L.I.

The recent researches of Bamberger (*Ber.*, 1894, 27, 1348 and 1548) and Wohl (*ibid.*, 1432) have shown that when nitrobenzene is reduced under certain conditions, β-phenylhydroxylamine is formed.

This compound is readily oxidised to nitrosobenzene, so that the latter, originally obtained as a green oil by Baeyer by the action of nitrosyl bromide on mercury diphenyl (*Ber.*, 1874, 7, 1638), can now be obtained in fairly large quantities. Baeyer showed that by the action of nitrosobenzene on aniline dissolved in acetic acid, azobenzene was formed.

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* Since sending in this paper, I have received a private communication from Professor Meldola in which he states that he has prepared metamidoazobenzene by the same method which I have employed. Professor Meldola has found that it is a coloured compound, and has the same properties as the substance described by me.

I would also call attention to the paper by Meldola and Burls (*Proc. Chem. Soc.*, 1893, 124, 126), which I had overlooked, in which they intimate their intention to study meta-azo-compounds, and describe metaphenolazo-α-naphthylamine; also to the paper by Meldola and Hanes (*Proc. Chem. Soc.*, 1894, 140, 140), in which metanitrobenzene-azo-α-naphthalene, metanitroamidoazobenzene and metanitroazobenzene are described.

The primary object of this research was to see if metamidoazobenzene could be obtained by the action of nitrosobenzene (1 mol.) on metaphenylenediamine (1 mol.), and thus throw some further light on the "quinonoid" structure of azobenzene proposed by Dr. Armstrong.

It is evident that if metamidoazobenzene is a coloured substance, then the colour of azo-compounds does not necessarily depend on their having a "quinonoid" structure, since metamidoazobenzene cannot possibly be constituted in this way.

Metamidoazobenzene was obtained, not, however, by the action of nitrosobenzene on metaphenylenediamine, but by the action of the former on metamidoacetanilide and the subsequent hydrolysis of the compound so formed. Metamidoazobenzene, prepared by a method given later, is an intense orange-coloured substance crystallising from light petroleum in silky needles.

The action of nitrosobenzene on substances containing an amido-group was then further investigated, and the results, as far as at present ascertained, are now brought together in this paper. All the azo-compounds prepared in this way are coloured, and crystallise well. The results of the investigation at present seem to show that nitrosobenzene only reacts well with those substances containing an amido-group which are feebly basic; if the substance is strongly basic, then the yield of azo-compound is very small. Thus paraphenylenediamine (1 mol.) reacts with nitrosobenzene (1 mol.) to form paramidoazobenzene, but the yield is very poor, whereas with paramidoacetanilide the yield of paracetylamidoazobenzene is very good. Again, the reaction between nitrosobenzene and metaphenylenediamine was tried under very many conditions, but nothing but a black, slimy tar was obtained; the reaction with metamidoacetanilide, however, gave a fairly good yield of metacetylamidoazobenzene, although not so good as with the isomeric para-compound.

β-Phenylhydroxylamine was prepared by the method of Wohl (*Ber.*, 1894, **27**, 1432). The average yield from several experiments was about 50 per cent. of the theoretical, when the alcoholic solution was distilled quickly under reduced pressure.

The β-phenylhydroxylamine was oxidised to nitrosobenzene by potassium dichromate and sulphuric acid (Bamberger, *Ber.*, 1894, **27**, 1555), and if this is done carefully and as near 0° as possible, the yield of crude nitrosobenzene is about 90 per cent. of the theoretical. The nitrosobenzene used in these experiments was obtained by steam distilling the crude oxidation product. It comes over as a green oil which solidifies to a white solid on cooling.

Metacetylamidoazobenzene.—This substance is prepared by the action of nitrosobenzene on metamidoacetanilide. The latter compound was prepared in the crystalline form by Dr. Lawson, who gives the following method of preparation:—Ten grams of metanitracetanilide are ground up in a mortar with 5 grams of iron dust, and the whole gradually dusted into 200 c.c. of boiling water made slightly acid with a few drops of acetic acid. The reduction takes about one hour, after which the mixture is diluted, made alkaline with ammonia, boiled, and filtered hot. The filtrate is evaporated to a syrup on a water bath, and crystallisation started by rubbing or with a crystal. The yield of metamidoacetanilide is practically theoretical.

Eight parts of metamidoacetanilide are dissolved in 10 parts of glacial acetic acid and 40 parts of ordinary spirit. The solution is cooled down to about +5° and then 6 parts of nitrosobenzene dissolved in 10 parts of glacial acetic acid and 40 parts of spirit, also cooled down to about +5°, are added. Reaction at once begins. the colour of the mixture becomes dark yellow, and there is a slight rise in temperature. The mixture is allowed to stand until, on diluting a drop with water, there is no longer any smell of nitrosobenzene. This usually takes about two hours. The solution is then poured on to powdered ice, and sodium carbonate solution gradually added until neutral. During this process, a black, tarry-looking substance gradually separates out. This is filtered off and dissolved in hot benzene, fractionally precipitated with light petroleum spirit, and the liquid decanted off from time to time as the tar separates out. In this manner a golden-yellow product was obtained, which, after repeated crystallisation from acetic acid, melted at 130—131°. The yield from 8 grams of metamidoacetanilide is about 5 grams. The substance crystallises from acetic acid in golden-yellow platey needles. It is readily soluble in ether, benzene, alcohol, chloroform, ethylic acetate, and acetic acid, almost insoluble in light petroleum. On hydrolysis with caustic soda, it gives metamidoazobenzene. Hydrolysis with hydrochloric or sulphuric acid gives aniline and metaphenylenediamine.

0·1664 gave 25·5 c.c. of moist nitrogen at 18·9° and 741·2 mm. N = 17·53 per cent.

0·1143 gave 17·5 c.c. of moist nitrogen at 16·8° and 737·4 mm. N = 17·56 per cent.

$C_{14}H_{13}N_3O$ requires N = 17·57 per cent.

Reduction of Metacetylamidoazobenzene.—Two parts of metacetylamidoazobenzene are ground up in a mortar with one part of iron dust, and the mixture is introduced into a flask with 50 parts of water. When boiling, about six drops of glacial acetic acid are added. This starts the reduction, and aniline begins to come off. The mixture is boiled as long as aniline continues to come off, water being added from time to time if necessary. When the reduction is finished, the mixture is diluted, made slightly alkaline with ammonia, filtered, and evaporated to dryness. It is then extracted with benzene, from which crystals of metamidoacetanilide (m. p. 87—89°) separate.

Metamidoazobenzene.—Five grams of metacetylamidoazobenzene are boiled with 40 c.c. of caustic soda solution (about 45 per cent. NaOH) for about two hours. During the ebullition the substance melts and the mixture is well shaken. On allowing the mixture to stand, the oil solidifies; from this the liquor is poured off, and the solid product repeatedly recrystallised from light petroleum spirit, from which it crystallises when pure in long, silky, orange needles, m. p. 56—57°. It is also readily soluble in alcohol, acetic acid, ethylic acetate, acetone, chloroform, benzene, and ether.

0·1729 gave 30·8 c.c. of moist nitrogen at 12·5° and 756·9 mm. = 21·25 per cent.

0·1401 gave 25·5 c.c. of moist nitrogen at 15·3 and 759·4 mm. = 21·49 per cent.

$C_{12}H_{11}N_3$ requires N = 21·31 per cent.

Action of Nitrosobenzene on Aniline.—Five parts of nitrosobenzene are dissolved in 15 parts of glacial acetic acid, and this solution is added to a solution of 5 parts of aniline in 10 of acetic acid. Reaction commences at once, and the temperature gradually rises to about 45°, but begins to fall as soon as the reaction is finished. On cooling, a mass of crystals separates out, which on recrystallising are found to be azobenzene, m. p. 68°. The yield is practically theoretical.

Action of Nitrosobenzene on Phenylhydrazine.—Nitrosobenzene reacts with about one-third of its weight of phenylhydrazine, the chief product of the reaction being azobenzene.

Ten grams of nitrosobenzene were dissolved in 30 grams of acetic acid, and to this solution phenylhydrazine was gradually added from a dropping funnel. The substances react at once, and a gas is evolved. When about 3 grams of phenylhydrazine have been added, the evolution of gas ceases. The gas was collected, and appeared to be all nitrogen. The product was diluted, when a black oil separated; this was extracted with ether and finally distilled; after the ether had distilled over, a small quantity of phenylcarbylamine came over, and finally the main bulk distilled; this was a red oil, solidifying on cooling. On recrystallising, it was found to be azobenzene. No other products of the reaction were isolated.

Action of Nitrosobenzene on Paramidoazobenzene. Formation of Diparadiphenyldisazophenylene, $C_6H_5{\cdot}N_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_5$.—Eight parts of paramidoazobenzene are dissolved in 40 parts of glacial acetic acid, and to the warm solution 4 parts of nitrosobenzene dissolved in 8 parts of acetic acid are added. The mixture is then warmed on a water bath for about a quarter of an hour at 70—80°. On allowing the mixture to stand, a red precipitate separates out, which on recrystallising from glacial acetic acid melts at 168—169°. The yield from 8 grams of paramidoazobenzene is 12 grams of diparadiphenyldisazophenylene. This substance crystallises from glacial acetic acid in small leaves; it is very slightly soluble in ether, benzene, alcohol, ethylic acetate, and hot petroleum spirit, more readily in hot acetic acid. On trying to prepare this substance by the action of 2 mols. of nitrosobenzene on 1 mol. of paraphenylenediamine nothing but a black-looking tar was formed, from which no crystalline substance could be obtained. Diparadiphenyldisazophenylene is a very stable substance, and very difficult to sulphonate. On warming it with 50 per cent. sulphuric anhydride for two days, the substance remained unchanged.

An attempt was also made to prepare the sulphonic acid by the action of nitrosobenzene on paramidoazobenzeneparasulphonic acid, but without success, although the experiment was tried in different solvents and under many conditions. Analysis of this substance gave the following numbers.

0·0962 gave 16·8 c.c. of moist nitrogen at 20° and 765·6 mm. N = 20·04 per cent.

0·1152 gave 19·3 c.c. of moist nitrogen at 17·9° and 766·4 mm. N = 19·68 per cent.

$C_6H_5{\cdot}N_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_5$ requires N = 19·58 per cent.

Reduction of Diparadiphenyldisazophenylene.—Five grams of the substance were ground up in a mortar with 3 grams of iron dust, and the mixture introduced into a flask with 50 c.c. of water. When boiling, a few drops of acetic acid were added, and the mixture boiled till there was no longer any smell of aniline. The mixture was then made slightly alkaline with ammonia, boiled, and filtered hot. The paraphenylenediamine in solution was identified by converting it into paraquinonedichlorimide, m. p. 134°, by Krausé's method (*Ber.*, 1879, 12, 47).

Action of Nitrosobenzene on Paratoluidine. Formation of Parabenzeneazotoluene.—Ten parts of nitrosobenzene are dissolved in 20 parts of glacial acetic acid, and to the solution 10 parts of paratoluidine in 10 parts of glacial acetic acid are added. The reaction commences at once, and the mixture must be kept cool. On standing, crystals of parabenzeneazotoluene separate out, and may be filtered with the aid of a filter pump and washed clean with a little dilute spirit.

On diluting the liquors with water, a further quantity of the product may be obtained. The yield of crude product is about 90 per cent. of the theoretical.

Parabenzeneazotoluene crystallises from dilute alcohol in beautiful, golden leaves, which, when pure, melt at 71—72°. It is readily soluble in chloroform, ether, light petroleum spirit, ethylic acetate, and benzene, but less readily in alcohol and acetic acid. On reduction with iron and acetic acid, it gives a mixture of aniline and paratoluidine. Parabenzeneazotoluene was also prepared by the action of paranitrosotoluene on aniline. The two products were identical in all respects. Analysis gave the following.

0·2495 gave 28·0 c.c. moist nitrogen at 12·5° and 757·4 mm. N = 14·35.
0 1426 ,, 17·4 ,, ,, 9·1° ,, 754·4 ,, N = 14·7.
$C_{13}H_{12}N_2$ requires N = 14·28 per cent.

Parabenzeneazotoluenesulphonic acid.—This substance is readily formed by the action of fuming sulphuric acid on parabenzeneazotoluene. Fifteen parts of the latter are dissolved in 60 parts of 100 per cent. sulphuric acid, and then 30 parts of 50 per cent. sulphuric anhydride added, and the mixture is heated on a water bath at 70—80° for about two hours. On pouring the mixture into water and allowing it to cool, the free acid separates out as a greenish mass of silky needles.

The sodium salt was prepared by boiling the sulphonated product with caustic soda and then adding sodium carbonate until just alkaline. When this is the case, the colour of the solution changes to reddish-yellow. On cooling, the sodium salt crystallises out in fine, reddish-yellow leaves, which can be recrystallised from hot water.

Analysis of the sodium salt gave the following numbers. The salt contains no water of crystallisation.

0·5275 gave 0·1256 Na_2SO_4. Na = 7·72.
0·2140 ,, 0·0501 ,, Na = 7 58.
$C_{13}H_{11}N_2SO_3Na$ requires Na = 7·72 per cent.

The *copper salt* of this acid is only slightly soluble in water, from which it crystallises in buff-coloured, microscopic leaves. The *silver salt* was prepared by adding silver nitrate solution to the sodium salt dissolved in water. It is sparingly soluble in water, and crystallises from it in orange-brown leaves

Parabenzeneazotoluenesulphonic Chloride.—Equivalent quantities of sodium parabenzeneazotoluenesulphonate and phosphorus pentachloride were mixed together in a dish. Action commences as soon as the mixture is warmed, and the whole melts and goes dark red. When the reaction was finished, the substance was allowed to cool when it again went solid; it was then powdered, washed well with water, and recrystallised from benzene, from which solvent it comes down in bright red prisms, m. p. 130—132°. It is also readily soluble in hot alcohol, acetic acid, ether, chloroform, and acetone, less soluble in petroleum spirit and ethylic acetate. A determination of chlorine by Carius' method gave the following result.

0·2164 gave 0·1073 AgCl. Cl = 12·27.

$C_{13}H_{11}N_2SO_2Cl$ requires Cl = 12·05 per cent.

Reduction of Sodium Parabenzeneazotoluenesulphonate.—Eight parts of the dry salt are dissolved in a small quantity of boiling water, and a few drops of acetic acid added. Three parts of iron dust are then gradually added. Boiling is continued until no more paratoluidine distils off, water being added, if necessary. The mixture in the flask is then diluted, made slightly alkaline with ammonia, boiled, and filtered. The filtrate was proved to contain parasulphanilic acid by converting the latter into parasulphobenzeneazo-β-naphthol and comparing this with the dye stuff obtained directly from β-naphthol and diazobenzenesulphonic acid.

Preparation of Parabenzeneazo-orthacettoluide,

$C_6H_3{\cdot}CH_3{\cdot}NHAc{\cdot}N{:}N{\cdot}C_6H_5$ ($CH_3 = 1$, $NHAc = 2$, $\text{-N:N-} = 4$).

—Ten parts of nitrosobenzene are dissolved in 20 parts of glacial acetic acid. Fifteen parts of paramido-orthacettoluide are dissolved in 20 parts of acetic acid. These solutions, when cold, are added one to the other and allowed to stand, when a solid, yellowish-brown mass separates out, which is filtered with the aid of a filter pump and washed with dilute spirit. The yield from 10 grams of nitrosobenzene is about 21 grams of the azo-compound.

Parabenzeneazo-orthacettoluide crystallises from alcohol in fine, light-yellow needles, and melts at 199°. It is readily soluble in alcohol, ethylic acetate, acetic acid, and hot benzene, but insoluble in ether, cold benzene, and light petroleum spirit. On hydrolysis, it gives metamidoparabenzeneazotoluene, and on reduction with iron and a small quantity of acetic acid, in the same way as that described for parabenzeneazotoluenesulphonic acid, it gives aniline and paramido-orthacettoluide.

Analysis of this substance gave the following numbers.

0·2329 gave 32·7 c.c. of moist nitrogen at 10·5° and 750·8 mm. N = 16·91.

0·0950 gave 13·5 c.c. of moist nitrogen at 11·0° and 755·4 mm. N = 17·04.

0·1469 gave 21·2 c.c. of moist nitrogen at 15·2° and 749·5 mm. N = 16·90.

$C_{15}H_{15}N_3O$ requires N = 16·54 per cent.

Hydrolysis of Parabenzeneazo-orthacetotoluide. Formation of Metamidoparabenzeneazotoluene, (CH_3 = 1, NH_2 = 2, –N:N– = 4.—Five parts of parabenzeneazo-orthacettoluide are boiled up in a flask with 20 parts of caustic soda, dissolved in a little water. The boiling is continued until the substance melts, when it forms a red oil on the surface of the soda. The mixture is shaken up well, and boiled for about a quarter of an hour, water being added if necessary. On diluting and cooling, the hydrolysed product forms a cake on the surface of the liquid. The latter is decanted off, and the solid product washed well with water, dried, and recrystallised from benzene. From this solvent it crystallises in intense yellow, microscopic needles, melting at 105—107°. It is readily soluble in acetic acid, chloroform, alcohol, ethylic acetate, and ether, less soluble in benzene, and very slightly in petroleum spirit.

Analysis gave the following results.

0·2078 gave 35·4 c.c. of moist nitrogen at 13·75° and 755·7 mm. N = 20·20.

0·1506 gave 24·5 c.c. of moist nitrogen at 7° and 765·0 mm. N = 20·03.

$C_{13}H_{14}N_3$ requires N = 19·91 per cent.

Preparation of Benzeneorthazo-orthacettoluide,

$C_6H_4 \cdot NHAc \cdot CH_3 \cdot N{:}N \cdot C_6H_5$ (NHAc = 1, CH_3 = 2, –N:N– = 3).

—This substance is prepared by the action of nitrosobenzene on orthamido-orthacettoluide, $C_6H_4 \cdot NH_2 \cdot CH_3 \cdot NHAc$ (CH_3 = 1, NHAc = 2, NH_2 = 6). Twenty grams of the latter are dissolved in 40 grams of glacial acetic acid, and this mixture added to a solution of 12 grams of nitrosobenzene in 20 grams of acetic acid. No apparent action takes place in the cold, but on warming to about 60°, and then allowing to stand, a beautiful, dark-red body crystallises out in fine needles, which, on recrystallising from dilute alcohol, melts at 194°. The yield of crude product is about 16 grams.

Benzeneorthazo-orthacettoluide is readily soluble in acetic acid, alcohol, ethylic acetate, and chloroform; less readily in benzene and ether; almost insoluble in light petroleum spirit.

On hydrolysis with caustic soda, it gave an oily substance, which was very difficult to obtain quite pure. On crystallising several times from benzene, and fractionally precipitating with light petroleum spirit, a product was obtained crystallising in rosettes of bright red, platey needles, and melting at 63—64°. This is probably metamidobenzeneorthazotoluene, $C_6H_4 \cdot NH_2 \cdot CH_3 \cdot N_2 \cdot C_6H_5$ (NH_2 = 1, CH_3 = 2, N:N = 3).

Benzeneazo-orthacettoluide, on reduction with iron dust, and a few drops of acetic acid, gave aniline and orthamido-orthacetotoluide

Analysis of the substance for nitrogen gave the following.

0·1468 gave 22 c.c. of moist nitrogen at 19·9° and 742·4 mm. N = 17·11.

0·1966 gave 27·5 c.c. of moist nitrogen at 19·1° and 765·6 mm. N = 16·52.

$C_{15}H_{15}N_3O$ requires N = 16·54 per cent.

The reactions between nitrosobenzene and bodies containing an amido-group are still being investigated, and the author hopes before long to publish further results.

In conclusion, the author begs to offer his thanks to Messrs. Brooke, Simpson, and Spiller, Limited, in whose laboratory at the Atlas Works, Hackney Wick, this investigation has been carried out.

Laboratory, Atlas Dye Works,
Hackney Wick, N.E.

XCIV.—*Some Derivatives of Maclurin.*

By Charles Samuel Bedford and Arthur George Perkin, F.R.S.E.

Some years ago, during some experiments with old fustic (*Morus tinctoria*), it was found by one of us that when an aqueous extract of this dye-stuff is treated with diazobenzene sulphate or other analogous substance, a new colouring matter is produced. As this was recognised to be of commercial value, the process was patented (C. S. Bedford, Eng. Pat. No. 12667, 1887), and the manufactured product is now known under the name of "Fustin."

The principal constituents of old fustic are, as is well known, morin, $C_{15}H_{10}O_7$, and maclurin, $C_{13}H_{10}O_6$, both of which are colouring matters, and investigation soon revealed the fact that the latter only is useful for this purpose. As the constitution of maclurin has lately been the subject of numerous investigations, and, moreover, as it is not generally known which of the constituents of old fustic form the basis of these new dye-stuffs, it appeared desirable to submit the subject to examination.

Benzeneazomaclurin.

To a slightly alkaline aqueous solution of maclurin, a solution containing diazobenzene sulphate (2 mols.) was added, causing the formation of a bright red precipitate. After standing a short time this was collected, washed with water, dried, and purified by crystallisation from nitrobenzene.

0·1056 gave 0·2460 CO_2 and 0·0393 H_2O. C = 63·52; H = 4·13.
0·1344 " 0·3126 " 0·0415 " C = 63·43; H = 3·84.
0·1467 " 16 c.c. N; $t = 25°$; bar., 745 mm. N = 11·97.
$C_{13}H_8O_6(N{:}N{\cdot}C_6H_5)_2$ requires C = 63·82; H = 3·82; N = 11·91 per cent.

It was therefore a compound of maclurin with 2 mols. of diazobenzene. When crystallised from nitrobenzene, it appears as a salmon-red mass of slender, hair-like needles, when from acetic acid, in the form of small needles, somewhat resembling alizarin in appearance. By the addition of alcohol to a boiling solution of this substance in a mixture of acetic acid and nitrobenzene, it is deposited on long standing as a beautiful, glistening mass of prismatic needles. It is very sparingly soluble in acetic acid, more readily in nitrobenzene, almost insoluble in alcohol and benzene. Dilute alkalis dissolve it with a bright, orange-red colour, and if these solutions are treated with zinc dust, reduction rapidly ensues with production of a pale yellow liquid. The barium salt produced by double decomposition forms orange-red flocks almost insoluble in water. The colouring matter dissolves in sulphuric acid with an orange-red colour. Attempts to produce a compound of maclurin with 1 mol. of diazobenzene were unsuccessful, in all cases the substance above described was produced, and the presence of free maclurin could be detected in the filtrate.

Orthotolueneazomaclurin was prepared from orthotoluidine and maclurin in a similar manner to the preceding compound. It was purified by crystallisation from nitrobenzene. On analysis,

0·1150 gave 0·2742 CO_2 and 0·0467 H_2O. C = 65·02; H = 4·51.
0·1345 " 13·4 c.c. N; $t = 23$; bar., 745 mm. N = 11·00.
$C_{13}H_8O_6(N_2{\cdot}C_6H_4{\cdot}CH_3)_2$ requires C = 65·06; H = 4·41; N = 11·25 per cent.

It was obtained as slender, hair-like needles, closely resembling the diazobenzene compound.

Paratolueneazomaclurin crystallised similarly. On analysis

0·1430 gave 14·6 c.c. nitrogen at 22°, and 762 mm. N = 11·59.
$C_{13}H_8O_6(N{:}N{\cdot}C_6H_4{\cdot}CH_3)_2$ requires N = 11·25 per cent.

Paranitrobenzeneazomaclurin, from paranitraniline and maclurin was obtained as a chocolate coloured mass, which crystallised from a mixture of nitrobenzene and acetic acid in spongy masses of very minute needles.

0·1155 gave 15·4 c.c. nitrogen at 23° and 745 mm. N = 14·72.
$C_{13}H_8O_6(N{:}N{\cdot}C_6H_4{\cdot}NO_2)_2$ requires N = 15 per cent.

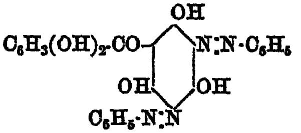
Maclurinazobenzeneparasulphonate of sodium.—To maclurin, dissolved in dilute alkali, a solution containing 2 mols. of diazobenzeneparasulphonic acid was added, causing the formation of an orange-red liquid. As this solution gave no precipitate when neutralised and saturated with common salt, it was, in the acid condition, treated with a large excess of this substance; an orange-red, tarry, resinous mass then separated. This product, when dissolved in a little hot water and treated with a small quantity of sodium carbonate solution, deposited an orange-red, crystalline precipitate, which was washed with a little water, followed by dilute alcohol, and recrystallised from water.

It formed an orange-red mass, seen under the microscope to consist of minute crystals. These were moderately soluble in water, almost insoluble in alcohol, and, when dry, possessed a beetle-green lustre. Analysis indicated that this substance consisted of the acid sodium salt, $C_{13}H_8O_6(N{:}N\cdot C_6H_4\cdot SO_3Na)_2$, but contaminated with a trace of a more alkaline salt. Owing to the somewhat poor yield obtainable of this substance, it was not found possible to isolate it in an absolutely pure condition without the use of considerably larger quantities of raw material than were at our disposal. By double decomposition it yields a barium salt in the form of an orange-red, amorphous precipitate, slightly soluble in water.

Maclurin, as is to be expected, yields colouring matters with diazoxylenes, tetra-azodiphenyl, and allied substances. The former closely resemble the diazobenzene derivative, and the latter is obtained as a chocolate-brown powder of a very insoluble nature.

Maclurin has been shown by König and Kostanecki (*Ber.*, 1893, **27**, 1994) to yield a pentabenzoyl derivative, $C_{13}H_5O(C_7H_5O)_5$, and, moreover, as it yields phloroglucin and protocatechuic acid by reduction or digestion with strong alkali, it appears to be an hydroxyketone, which may be represented thus, $C_6H_3(OH)_2\cdot CO\cdot C_6H_2(OH)_3$.

Experiments showed that protocatechuic acid does not combine with diazobenzene, whereas from phloroglucin, Weselsky and Benedikt (*Ber.*, 1879, **12**, 226) have obtained benzeneazophloroglucin $(OH)_3C_6H(N{:}N\cdot C_6H_5)_2$. It is, therefore, most probable that in benzeneazomaclurin, both diazobenzene molecules are united with the phloroglucin nucleus, the formula of the substance being consequently



It is interesting to note that catechin yields a compound with diazobenzene, $C_{18}H_{16}O_8(N_2\cdot C_6H_5)_2$ (Etti, *Monatsh.*, 1881, **2**, 252), and that the substance termed cyanomaclurin which is present with morin in jack wood gives a similar substance, $C_{15}H_{10}O_6(N_2 \cdot C_6H_5)_2$ (Perkin and Cope, this vol., p. 942). Our experiments have shown also that aqueous extracts of some tannin substances yield new compounds in this way, and it is known that these contain substances allied most probably to maclurin and catechin. Experiments with quercetin, fisetin, and morin, showed that they behave towards diazobenzene somewhat differently, though, like maclurin and catechin, all yield phloroglucin as one of the products of their decomposition with alkali. When treated in alkaline solution with diazobenzene sulphate, they yield deep *brown* precipitates, though with some difficulty, and these possess little tinctorial value. It is possible that these reactions are characteristic of the above two classes of natural products, the *red* coloured easily formed dye-stuffs being produced from derivatives of the benzophenone class, whereas the brown indicate the presence of the xanthone or phenylated γ-pyron group.

Dyeing Properties.

As is to be expected from their constitution, benzeneazomaclurin and its homologues, dye wool and silk, both alone and with the aid of mordants. By the former method, using a slightly acidified bath, shades are obtained which vary from a light orange to a brown colour according to the strength of the solution. On striped mordanted calico there is obtained with aluminium mordant, orange-red, and, with iron mordant, pale olive to deep brown shades, and closely similar results are obtainable with wool and silk in the same manner. With chromium mordant upon wool and silk, the results resemble those obtained with unmordanted fabrics, the colours, however, being deeper and of greater utility. The benzeneazo-, ortho-, and paratolueneazo-, xyleneazo-, and paranitrobenzeneazo-derivatives of maclurin yield very similar colours; the shades become, however, redder in tone in the order in which they are here placed. By the action of soap the colours obtained are at first slightly impoverished, but further treatment has but little action.

The acid sodium salt of maclurinazobenzeneparasulphonic acid dyes unmordanted wool and silk orange-yellow to orange coloured shades.

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XCV.—*The Constituents of* Artocarpus integrifolia. Part I.

By Arthur George Perkin, F.R.S.E., and Frank Cope.

Artocarpus integrifolia is the well-known jack-fruit tree, belonging to the *Urticaceæ*, a large tree cultivated throughout India, Burmah, and Ceylon, except in the north. When freshly cut, the heart-wood is yellow, but this, on long exposure to air gradually darkens, finally becoming of a mahogany colour. It is largely used for carpentry, furniture, &c., being considered one of the most handsome furniture woods used in the country, and is stated to be exported to Europe for this purpose. The rasped wood is used by the natives of India and Java as a yellow dye, in conjunction with alum, for colouring the robes of the Burmese priests, also for dyeing silk, and for general purposes.

A sample of this wood was brought to England by Mr. John Ingleby, late Chief Surveyor* of the Northern and North Central Provinces of Ceylon, who introduced it to the notice of Messrs. Wood and Bedford, of Leeds. This firm being anxious to test its utility as a dye-stuff, and, moreover, being struck by its resemblance to old fustic (*Morus tinctoria*), imported a considerable quantity from Ceylon, and to them our best thanks are due for a supply of material for the carrying out of this investigation.

A characteristic property of this dyewood, by which it may be distinguished from either old fustic or any other natural yellow dyestuff that has come under our notice, is as follows. If an aqueous decoction be treated with dilute alkali, a yellow solution is obtained, and this, if gently warmed, assumes a beautiful blue tint, which, on standing, rapidly becomes green, and finally brown-yellow.

The Colouring Matter. Morin.

The ground wood was extracted for six hours with 10 times its weight of boiling water, and the light brown extract, while still hot, treated with lead acetate solution as long as a precipitate was formed. After standing some hours, this was collected, washed with water, and the filtrate placed aside for subsequent examination. The lead compound, being made into a thin cream with water, was run in a fine stream into boiling dilute sulphuric acid, an orange-brown liquid resulting, which contained in suspension a small quantity of a sticky, resinous substance. As the latter had the effect of greatly retarding the subsequent filtration, the boiling mixture was treated with some quantity of barium chloride solution, the precipitated barium sulphate formed carrying down with it this impurity, which could now be readily removed by the use of a hot-water filter. The filtrate was extracted with a large volume of ether, the extract evaporated, the brown, semi-crystalline residue thus obtained dissolved in a little acetic acid, and the solution treated with three times its volume of boiling water. On cooling, a light-coloured, crystalline product separated, and this was collected, washed with dilute acetic acid, and recrystallised in a similar manner until colourless.

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* Indian Civil Service.

0·1254 dried at 160° gave 0·2740 CO_2 and 0 0394 H_2O. C = 59·59; H = 3·49.

$C_{15}H_{10}O_7$ requires C = 59·60; H = 3·31 per cent.

Thus obtained, it appeared as a mass of colourless, glistening needles, readily soluble in alcohol and acetic acid, somewhat sparingly in ether, and melting with decomposition at about 300°. Solutions of the alkalis dissolved it with a yellow colour, and if these liquids were treated with excess of alkali, crystalline salts were deposited in the form of slender needles. The barium and lead compounds were obtained as orange coloured, amorphous precipitates insoluble in water. Sulphuric acid dissolved the substance $C_{15}H_{10}O_7$ with a yellow colour, and addition of ferric chloride to its alcoholic solution caused the formation of a green liquid. It dyed mordanted calico with shades which appeared identical with those given by morin, one of the colouring matters of old fustic (*Morus tinctoria*), and as, moreover, both substances, when treated with sodium amalgam in alcoholic solution, yielded a characteristic deep green liquid, it appeared probable that they were identical. When heated they behaved similarly, and when destructively distilled both yielded a small quantity of a sublimate, crystallising from water in the form of minute yellow needles, which had the properties of Benedikt's paramorin (*Ber.*, 1875, 8, 606).

In a former communication (Perkin and Pate, this vol., 649) it was shown that though morin yielded acid compounds very similar to those produced from quercetin and other allied colouring matters, it differed from these in that during the formation of its sulphuric acid compound 1 mol. of water is eliminated. In order, therefore, to be quite certain that the colouring matter of jack-wood was really morin, its solution in boiling acetic acid was treated with sulphuric acid. On cooling, an orange-red, crystalline mass separated, which was collected, washed with acetic acid, and dried at 110°.

0·1382 gave 0·2388 CO_2 and 0·0400 H_2O. C = 47·12; H = 3·21.

$C_{15}H_8O_6,H_2SO_4$ requires C = 47·11; H = 2·62 per cent.

The hydrobromic acid compound, obtained in a similar manner was also analysed.

0·1348 gave 0·2312 CO_2 and 0·0378 H_2O. C = 46·77; H = 3·12.

$C_{15}H_{10}O_7$,HBr requires C = 47 00; H = 2·84 per cent.

The composition of the sulphuric acid compound, and a comparison of this and the hydrobromic acid derivative with those of morin obtained from old fustic, left no doubt as to their identity. The colouring matter of jack wood is therefore *morin.*

Cyanomaclurin.

The aqueous filtrate from the lead compound of morin was treated with sulphuretted hydrogen, the lead sulphide filtered off, and the nearly colourless filtrate evaporated over the steam bath. During this operation, it became gradually darker, and, as a final result, a thick, sticky mass of a deep brown colour was obtained. Subsequently it was found preferable to discontinue the evaporation before complete dryness, for by this means the production of this dark-coloured product, the result of a decomposition, was partially avoided. To the liquid, a large quantity of common salt was now added, causing the precipitation of a sticky, brown product, which was removed by filtration through calico, and the resulting nearly colourless filtrate extracted with much ethylic acetate, and the extract evaporated. As the solution became concentrated, crystals separated out, a semi-solid, pasty mass being obtained on cooling; this was thrown upon calico, squeezed to remove an adhering sticky substance, and finally strongly pressed. To purify this product, it was again dissolved in ethylic acetate, the solution evaporated to crystallisation, the residue mixed with some quantity of acetic acid, and filtered by means of the pump. By washing with small quantities of acetic acid, followed by chloroform, a colourless mass was obtained, which, if necessary, could be further purified in a similar manner.

0·1209 dried at 160° gave 0·2769 CO_2 and 0·0463 H_2O. C = 62·46; H = 4·25.

0·1170 dried at 160° gave 0·2688 CO_2 and 0·0459 H_2O. C = 62·65; H = 4·35.

$C_{15}H_{16}O_7$ requires C = 62·79; H = 4·65 per cent.
$C_{15}H_{12}O_6$,, C = 62·50; H = 4·16 ,,

It formed a colourless mass of minute prisms, which when heated commence to darken at 200°, and decompose rapidly at about 250°. Though it does not separate from its solutions in alcohol or acetic acid on cooling, it does not appear to be readily soluble in these liquids, prolonged boiling being frequently necessary to effect this object. From dilute acetic acid or water itself, however, it is deposited, after standing several days, in prisms closely resembling cane sugar in appearance. It does not dye with mordants. Sulphuric acid dissolves it, forming a beautiful, crimson solution, and with nitric acid a red-brown liquid is produced, which, on standing, gradually becomes of a scarlet tint. Ferric chloride colours its aqueous solution violet. With lead acetate, it yields no precipitate, but with basic lead acetate, a colourless, insoluble compound is formed. Most characteristic is its reaction with dilute alkalis, for if but a trace be warmed with these liquids, a beautiful, deep indigo-blue solution rapidly forms, which, on longer digestion, passes into green, and finally brown-yellow. This, by neutralisation with acid, yielded no precipitate, and when extracted with ether and evaporated, a sticky, brown residue was obtained, from which at present we have been unable to isolate any crystalline product. On account of its above-described property, and as it stands to jack-wood in the place of the maclurin of old fustic, we propose for the name of this substance *cyanomaclurin*.

When an aqueous solution is boiled with dilute mineral acids, various substances appear to be formed, varying in property according to the length of the digestion, and resembling closely in appearance the so-called anhydrides of catechin (Etti, *Annalen*, 1877, **186**, 332). The first product of this reaction separates out, on cooling, as a reddish-brown precipitate, sparingly soluble in water, and readily in dilute alkali, but as the digestion proceeds this is by degrees rendered more insoluble, there being finally obtained a red-brown powder insoluble in alkalis and solvents. As is well known, this reaction is characteristic of numerous tannin substances, and though cyanomaclurin is not a tannin matter, in that it does not coagulate albumin solution, it is evidently allied to catechin, maclurin, and other substances of this tannin class.

It has been shown that various so-called "tannic acids," among others China- and chinovatannic acids (Rembold, *Annalen*, 1867, **143**, 270), and filix-tannic acid (Malin, *ibid.*, 276), when digested with acid, are decomposed into an insoluble red substance and a sugar, being thus probably glucosides. Experiment showed that by this reaction no sugar was obtained from cyanomaclurin, and that the amount of final red product produced was equal to 85—90 per cent. of the weight of the original substance.

The alteration in colour of the freshly cut wood from a yellow to a mahogany tint on long keeping, and the sticky, red-brown substances obtained during the preparation of cyanomaclurin (p. 939), are evidently the result of the production of one or other of its above-described decomposition products.

Examination by Zeisel's method showed that it contained no methoxy groups.

Action of Fused Potash.—In studying this decomposition, the substance was heated with 10 parts of potassium hydroxide and a little water, at 150—180°, for about three quarters of an hour. The dark coloured solution at first formed rapidly became brown, gas being evolved, and the operation was discontinued when this had considerably moderated. The melt was dissolved in water, the solution acidified, extracted with ether, the extract evaporated, and the brown, sticky residue allowed to stand for some hours over sulphuric acid. Crystals were gradually deposited, and these were drained upon a porous tile, and purified by two or three crystallisations from water. The product consisted of nearly colourless needles melting at 208—209°, an aqueous solution of which, when treated with ferric chloride, gave a blue-violet coloration. Sufficient of this substance could not be obtained for analysis, but its reactions agree closely with those given for cresorcincarboxylic acid (methyldihydroxybenzoic acid) [$COOH : OH : OH : CH_3 = 1:2:4:5$], with which it is probably identical. The yield is exceedingly small, but we hope by working with large quantities of cyanomaclurin to analyse the substance and confirm its identity.

In order to determine if this was the sole product of the reaction, a second experiment was made as follows. The residue from the ethereal extract of the melt was dissolved in water, and a sample treated with lead acetate solution; by this means only a minute amount of a dirty-coloured precipitate was obtained, too small to repay investigation.

To the main portion of the solution, barium carbonate was added to neutralise the acid previously shown to be present, the whole extracted with ether, and the extract evaporated. As the brown residue obtained showed no signs of crystallisation, it was digested for some hours with boiling toluene, and the solution treated with animal charcoal. Colourless, prismatic needles separated out on cooling, which were collected and recrystallised from toluene. This product melted at 103—104°, gave with lead acetate no precipitate, and with ferric chloride solution a faintly green coloration. Unfortunately the yield obtained was too small to allow of the certain identification of this substance, but in its properties it most nearly approaches those assigned to cresorcin (methyldihydroxybenzene; $CH_3{\cdot}OH{\cdot}OH = 1 : 2 : 4$). For its investigation, considerable quantities of cyanomaclurin will be required, and as soon as this can be obtained, work in this direction will be continued.

Action of Diazobenzene.—From the results of the study of the reaction of diazobenzene with maclurin (C. S. Bedford and A. G. Perkin, this vol., p. 933), it seemed probable that the former might also combine with cyanomaclurin, and experiment soon proved this to be the case. An aqueous solution of cyanomaclurin, to which some potassium acetate had been added, was treated with a solution of about 2 mols. of diazobenzene sulphate, and the bright scarlet precipitate thus formed collected, washed with water, and dried. For purification, it was crystallised from alcohol, a hot solution of which deposits it somewhat slowly in spongy masses of needles.

0·1050 dried at 160° gave 0·2507 CO_2 and 0·0422 H_2O. C = 65·11; H = 4·46.

0·1199 dried at 160° gave 0·2863 CO_2 and 0·0486 H_2O. C = 65·12; H = 4·50.

0·1272 dried at 160° gave 12 c.c. of nitrogen at 20°, and 762 mm. N = 10·92.

$C_{15}H_{10}O_6(C_6H_5N_2)_2$ requires C = 65·32; H = 4·03; N = 11·29 per cent.
$C_{18}H_{14}O_7(C_6H_5N_2)_2$ „ C = 65·21; H = 4·34; N = 10·14 „

It was evidently a compound of 2 mols. of diazobenzene with cyanomaclurin. It forms a scarlet, glistening mass, somewhat sparingly soluble in alcohol, but very considerably more soluble in the usual solvents than the corresponding maclurin derivative. Dilute alkalis dissolve it with an orange-red colour, and these solutions, when treated with zinc dust, are reduced with the production of pale yellow liquids. It dyes unmordanted wool and silk, in a slightly acid bath, orange-yellow shades, very similar to those obtained with the maclurin compound, but, as was to be expected, it does not combine with mordants.

The analysis of cyanomaclurin agrees well, as shown above, with either of the two formulæ $C_{15}H_{12}O_6$ and $C_{18}H_{16}O_7$, whereas that of its diazobenzene compound, judging by the percentage of nitrogen, agrees somewhat more closely with the former, which is probably the correct one. Both are interesting as they tend to show a connection with either morin, $C_{15}H_{10}O_7$, or catechin, $C_{18}H_{18}O_8$, and with both these substances it has points in common.

Attempts to prepare acetyl and other derivatives have yielded at present unsatisfactory results, and this is no doubt due to its instability in the presence of most reagents. It is our intention to continue the study of this most interesting substance, but this work will of necessity be slow, for its isolation from the dyewood in any quantity will entail considerable time and labour.

As morin has been previously only known to exist in old fustic, and as this dye-stuff contains also a second colouring matter, maclurin, it was necessary to determine whether the latter also existed in jack wood. Various tests, however, showed no indication of the presence of this substance; but in order to be quite certain, it seemed best to prove this indirectly by examining old fustic according to the methods employed with jack-wood.

A boiling aqueous extract of old fustic was therefore treated with lead acetate, the precipitate collected, and the filtrate, after removal of lead in the usual manner, evaporated to a small bulk. The dark-coloured liquid thus obtained was treated with excess of salt, filtered, the filtrate extracted with ethylic acetate, and the extract evaporated. The resulting sticky product showed no signs of crystallisation, and it was therefore dissolved in dilute acetic acid and allowed to stand some hours. A light yellow precipitate gradually separated, which was collected and purified by crystallisation in a similar manner, and this was found from its dyeing and other properties to be identical with maclurin. With lead acetate solution, it yielded a precipitate, but was not entirely thrown down in this way, and its isolation from old fustic in the above manner is due to the fact that its lead compound at first formed, is partially decomposed by the acetic acid which is simultaneously liberated from the lead acetate. On the other hand, morin is entirely precipitated by this reagent.

Jack-wood thus treated as here shown yields no substance having the properties of maclurin, and its non-existence in this dye-stuff is thus conclusively proved. Morin is consequently the sole colouring matter of jack-wood, and the cyanomaclurin which it contains occupies the place of the maclurin in old fustic.

As the dilute acetic acid filtrate from the precipitated maclurin (see above) appeared to contain a second substance, it was evaporated to dryness, a dark-coloured sticky residue being thus obtained. When boiled with dilute alkalis, an aqueous solution of this product darkened somewhat in colour, but did not yield the characteristic blue tint formed when cyanomaclurin is thus treated. In a similar manner to the latter, however, it was decomposed by boiling dilute acids with formation of a red-brown precipitate, and evidently consisted of a substance not hitherto known to exist in old fustic. It gives no precipitate with lead acetate solution, and is therefore distinct from the tannic acid which, according to Löwe (*Fresenius Zeitschrift für Analytische Chemie*, **14**, 127), is present in this dye-stuff in conjunction with morin and maclurin. This substance will be submitted to examination.

Dyeing Properties.

As was to be expected from the results of its chemical examination, jack-wood dyes shades very similar to those of old fustic, that is, olive-yellow with chromium, dull yellow with aluminium, and a brighter yellow with tin mordant. The results obtained, however, are somewhat disappointing when it is considered that its sole colouring matter is morin, for this by itself dyes fine bright shades, whereas those yielded by the wood are duller in comparison. This must be accounted for as due to the brown decomposition products of cyanomaclurin which are probably formed to a slight extent during the dyeing operation, and also exist in the free state in the dye-stuff itself.

Experiments showed that the sample of jack-wood here examined contained only about one-third of the colouring matter of old fustic. It is, however, probable that this represents a poor quality, for that brought originally from Ceylon by Mr. J. Ingleby was found equal to old fustic in dyeing power.

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XCVI.—*Optically Active Methoxy- and Propoxy-succinic Acids.*

By Thomas Purdie, F.R.S., and Herbert William Bolam, B.Sc.

It has been shown in previous communications to this Journal (Trans., 1893, 63, 217—229) that the alkyloxysuccinic acids produced by the addition of the elements of alcohols to fumaric and maleic acids are capable of being resolved into optically active components, the resolution of methoxysuccinic acid having been effected by the fractional crystallisation of the cinchonine salt, and that of ethoxysuccinic acid by the action of *Pencillium glaucum.* As the alkyloxysuccinic acids are of considerable interest from their bearing on quantitative problems relating to optical activity, the present research was undertaken with the object of finding a more advantageous method of resolving methoxysuccinic acid; also of preparing and resolving into its active components the corresponding propoxy compound. The active methoxysuccinic acid obtained in the course of the investigation was employed for determining the specific rotation of the compound in more concentrated aqueous solutions than were formerly used, and in organic solvents. We succeeded also in procuring a sufficient quantity of the active propoxysuccinic acid to compare the activity of the acid itself and of some of its salts with that of the corresponding methoxy and ethoxy compounds.

Resolution of Methoxysuccinic acid.

The acid used in our experiments was prepared from methylic fumarate by methods already described (*loc. cit.*). The method of resolution by means of the cinchonine salt as previously carried out, had yielded active acids more or less contaminated with inactive racemoid acid, from which the former had to be afterwards freed; before attempting other methods of resolution, the same process was repeated, in order to see whether a more careful recrystallisation of the cinchonine salt would give a more active product, and possibly increase the yield of active material.

Two hundred and ninety-two grams of cinchonine were dissolved in 300 c.c. of a slightly warmed aqueous solution containing 146 grams of the acid. In the course of 24 hours, the solution deposited a hard cake of crystalline needles, from which, after four recrystallisations from water, 110 grams of the dry cinchonine salt of the dextrogyrate acid were obtained, that is to say, about half the calculated quantity supposing the separation to have been complete. The salt was decomposed with barium hydroxide, and the barium salt converted into acid as previously described. On evaporating the solution of the barium salt, it formed a gelatinous mass, without depositing any of the less soluble inactive salt, as was the case in former experiments. The active acid was converted into acid potassium salt, which was crystallised fractionally. Four successive fractions gave in aqueous solution the specific rotations +22·47°, 23·09°, 23·16°, and 23·23° ($c = 8$, $l = 2$, $t = 15$—18°), and the first of these on being recrystallised gave +23·13°, numbers almost identical with the specific rotation of the salt prepared in the previous research, which was +23·26° for similar concentration. It appears, therefore, that the hydrogen potassium salt formerly obtained was practically pure, the racemoid compound which was present in considerable quantity in the crude product from the cinchonine salt having been removed subsequently by the fractional crystallisation of the barium salt and of the acid potassium salt itself. That the cinchonine salt of the dextrogyrate acid from the first crystallisation is mixed with a considerable quantity of the salt of the oppositely active acid is proved by our observations on the mother liquors resulting from its recrystallisation; the first of these gave in fact an acid potassium salt of the lævogyrate acid, successive fractions of which showed the specific rotations —21·92° and —22·13°, and even the third mother liquor gave a considerable quantity of inactive barium salt.

The main portion of the lævogyrate acid was contained in the uncrystallisable mother liquor from which the cinchonine salt had been deposited, but mixed, as in former experiments, with much of the oppositely active component. The syrup referred to was treated in the same way as the crystallised cinchonine salt; the barium salt solution deposited much of the racemoid salt, which was filtered off. The successive fractions of hydrogen potassium salt finally obtained gave the specific rotations −22·39°, −22·96°, and −23·18° under the conditions mentioned above. The active acids resulting from the acid potassium salts were dried in a vacuum, and gave the following results on analysis. I. *d*-acid. C, 40·37 per cent.; H, 5·48 per cent. II. *l*-acid. C, 40·52 per cent.; H, 5·41 per cent. Calculated: C, 40·54 per cent.; H, 5·41 per cent. Observations on the activity of these acids are given later.

Resolution by Strychnine.

As the purification of the cinchonine salt by recrystallisation had not increased the yield of the active acids, resolution by means of the strychnine salt was resorted to. Fifteen c.c. of an aqueous solution containing 1·64 grams inactive methoxysuccinic acid dissolved when slightly warmed 6·68 grams of the alkaloïd, the calculated weight for the normal salt being 7·4 grams. The solution deposited crystals of two kinds, hard transparent plates and opaque silky needles. It was found that by crystallising from a more dilute solution and adding successively nuclei of the two kinds of crystals, the solution could be made to deposit the plates first, and then the needles. 2·6 grams of the plates gave after removal of the strychnine with ammonia 10 c.c. of a solution which showed a rotation of −56′ in a 200 mm. tube. It appeared, therefore, that from a neutral solution, the normal salt of the lævo-acid was first deposited. The normal salts showed, however, a great tendency to crystallise simultaneously even when crystallisation was induced by a nucleus of one of them, and their separation was difficult.

With the view of deciding on the best method of effecting the resolution, the normal and acid strychnine salts of both active acids were prepared, the acids already obtained by the cinchonine method being used for the purpose. The following observations were made. *Normal dextro-salt*—long thin needles; crystallises readily. *Acid dextro-salt*—bundles of opaque radiating needles, much more soluble than any of the other salts. *Normal lævo-salt*—glassy square plates, more insoluble than either of the preceding. *Acid lævo-salt*—plates like the normal lævo-salt, but apparently more soluble. It seemed, therefore, best to remove the lævogyrate acid first as acid salt, and then the dextrogyrate acid as normal salt.

Twenty-three grams of strychnine were accordingly dissolved in an aqueous solution containing 10·4 grams of inactive methoxysuccinic acid, the quantities used being in molecular proportions. The solution, having been sown with acid lævo-salt, deposited a crop of plates, weighing 8 grams, in the course of 24 hours, and the mother liquor deposited, on evaporating, a further crop of the same salt, weighing 5·5 grams. The 13·5 grams gave on recrystallisation 10·8 grams of the dry salt, which was dissolved in water and decomposed by adding ammonia. The strychnine, which was separated by filtration and dried, weighed 6·77 grams, the calculated quantity for the acid salt being 7·48 grams. The ammoniacal solution having been evaporated to a small bulk, a little more strychnine separated, which was filtered off; the filtrate, being made up to 50 c.c., gave the rotation −1·74° in a 200 mm. tube. The mother liquor, from which the acid lævo-salt had been removed, was neutralised by warming slightly with excess of strychnine; the filtered liquid, having been sown with a nucleus of dextro-normal salt, gave a crop of long, thin needles, which, after being recrystallised twice from water and dried, weighed 15·2 grams. The ammoniacal solution, obtained as before from this salt, gave the rotation +59′ in a 200 mm. tube.

The acid, having been evidently resolved into its optically active components by the process described, the experiment was carried out on a larger scale, 73 grams of acid being used and 167 grams of strychnine. The acid lævo-salt obtained was recrystallised twice from water, and then weighed in the dry state 73 grams. It gave on decomposition with ammonia 47 grams of strychnine, the calculated quantity for the acid salt being 50·6 grams. The calcium salt was obtained from the solution of the ammonium salt by treatment with calcium hydroxide, removal of the excess of the latter by means of carbonic anhydride, and evaporation of the filtered liquid. To insure the removal of traces of strychnine, the dry calcium salt was digested repeatedly with alcohol, and, to separate the active salt from any of the less soluble racemoid form with which it might be contaminated, it was finally kept in agitation with a quantity of cold water insufficient for complete solution. The acid was obtained by adding the calculated quantity of sulphuric acid to the solution of the calcium salt, and by extracting the residue left on evaporating the filtered liquid with alcoholic ether. The acid obtained weighed 15 grams; being slightly coloured, it was converted into the acid potassium salt, from which the colouring matter was removed by digestion with alcohol. An estimation of potassium in the salt dried at 100° gave 21·14 per cent., the calculated percentage being 21·01. The salt being recrystallised from water, two successive crops of crystals showed the same specific rotation, namely, −23·12° ($c = 8$, $t = 15°$), that of the purest salt obtained by the cinchonine method being −23·18° under similar conditions.

The normal strychnine salt of the dextrogyrate acid obtained by neutralising with strychnine the mother liquor, from which the acid salt of the lævogyrate acid had been separated, weighed 125 grams after being recrystallised twice from water, and gave

100 grams of dry strychnine when decomposed with ammonia, the calculated weight of strychnine for the normal salt being 102 3 grams. The dextro-acid, weighing 10 grams, was obtained by the same process as the lævo-acid, and was similarly converted into the acid potassium salt; an estimation of potassium in the latter gave 20·94 per cent., the calculated percentage being 21·01, and the specific rotation of the salt was +23 05° under the conditions mentioned above; a second fraction gave the number +22·75°; but as it was obtained by evaporating the solution to a very small bulk, the lower activity may be accounted for by the presence of active normal salt. The experiments which have been described show that methoxysuccinic acid can be resolved into its active components with the aid of strychnine in two ways, namely, as normal salt, in which case the salt of the lævo-acid separates first from the solution, or as acid salt when the salt of the lævo-acid crystallises first, the dextro-acid being afterwards obtained as normal salt.

Pure optically active products can be got by both the cinchonine and strychnine methods. The latter process is however to be preferred, as the strychnine salts of both active acids being readily crystallisable, they can be more easily isolated in the pure state than the cinchonine salts. With the experience already obtained, the yield of active acid obtainable by the strychnine method might, we believe, be much increased. In the experiment described above, of the 73 grams of inactive acid only about 22 grams each of the dextro- and lævogyrate components were removed as strychnine salt, the rest being left in the mother liquor, mostly in the form of normal salt. An attempt was made to resolve the acid in the collected mother liquors, after neutralising them completely with strychnine, by fractional crystallisation of the normal salts, but the separation of the two forms was incomplete, and the yield of active acid small. The acid might, however, be recovered from the solutions, and the process of resolution then carried out as described.

In the table below we give the results of our observations on the optical activity of solutions of the methoxysuccinic acids in water, acetone, and ethylic acetate, the material used being that obtained by the cinchonine method. The most concentrated solutions were made by dissolving weighed quantities of the acid, dried in a vacuum till constant, and making up to a known volume, and the other solutions were prepared by diluting aliquot parts of these solutions to known volumes. The observations were taken in a 200-mm. tube at the temperatures mentioned.

	Dextro-acid.				Lævo-acid.			
Solvent.	$t.^\circ$	$c.$	$a.$	$[a]_D$.	$t.^\circ$	$c.$	$a.$	$[a]_D$.
Water........	15	24·6520	16·07°	+32·59°	15	22·0353	14·41	−32·70
„	14	16·6805	10·94	+32·79	—	—	—	—
„	15	8·7620	5·73	+32·70	15	7·9266	5·14	−32·42
Acetone	11	24·9640	28·51	+57·10	11	25·5833	28·78	−56·25
„	11	18·7693	21·88	+58·29	13	15·6140	18·17	−58·18
„	14	10·2960	11·95	+58·03	—	—	—	—
„	14	4·1184	4·90	+59·49	—	—	—	—
„	14	1·6474	1·98	+60·09	—	—	—	—
Ethylic acetate.	11	20·5424	26·08	+63·48	11	25·5510	31·63	−61·90
„ .	12	15·8720	20·46	+64·45	13	19·0770	24·01	−62·93
„ .	12	8·9193	11·53	+64·64	—	—	—	—

Preparation of Inactive Propoxysuccinic acid.

This acid was prepared in two ways, namely, from maleïc anhydride and from propylic fumarate. A solution of 53 grams of maleïc anhydride in an equal weight of propylic alcohol was heated on a water bath so as to convert the anhydride into acid ethereal salt, and the mixture was added to 300 grams of the same alcohol in which 25 grams of sodium had been previously dissolved, the proportions being 1 mol. of the anhydride to two atoms of sodium. The resulting solution, after being heated for some time on the water bath, was mixed with water and again heated until the ethereal salt which had been formed was hydrolysed, and the solution was then strongly acidified with hydrochloric acid, which precipitated some fumaric acid. On adding calcium chloride to the filtered and neutralised solution, and boiling, a very slightly soluble calcium salt was precipitated which, after being washed and dried at 100°, gave the following results on analysis:—

I. 0·5765 gave 0·2645 $CaCO_3$. Ca = 18·35.
II. 0·6201 „ 0·1605 CaO. Ca = 18·49.
Calculated for $C_7H_{10}O_5Ca$, 18·69 per cent.

Calcium propoxysuccinate precipitated as described is anhydrous.

The salt was converted into acid by treating it with the calculated quantity of sulphuric acid and extracting the residue left, after evaporation of the filtered liquid, with alcohol. The acid, which remained as a coloured syrup after evaporating the alcohol, was dissolved in ether, which left the colouring matter undissolved. The acid from the ethereal solution gradually solidified on standing over sulphuric acid; but, as it was still contaminated with some viscous matter, it was converted into lead salt by neutralization with ammonia, and precipitation with lead nitrate, and from the lead salt the acid was recovered in the usual manner by the action of sulphuretted hydrogen. The acid now crystallised in wartlike groups, and had the melting point 73—75°. The substance was still, however, not quite pure, analysis giving the percentages 6·86 and 46·69 for hydrogen and carbon respectively, instead of 6·82 and 47·73. To assure ourselves that the acid had not suffered decomposition, part of it was converted into calcium salt by neutralization with calcium carbonate in very dilute solution. An estimation of calcium as sulphate in this salt gave 18·66 per cent., and a combustion gave the following results:—Found, C = 39·12, H = 4·59, Ca = 18·82; calculated, C = 39·25, H = 4·67, Ca = 18·69 per cent.

The following observations were made on other salts of the acid:—The acid potassium salt formed a thick syrup which crystallised very imperfectly; the acid ammonium salt crystallised from a syrup in needles; the zinc salt crystallised from a concentrated solution in very deliquescent needles. The barium salt crystallised in the form of hydrated, glistening scales, more soluble in cold than in hot water. This salt does not become anhydrous till heated to 130—150°, and it begins to decompose at 180°; the estimation of water of crystallisation on the air-dried salt, as in the case of the corresponding ethoxysuccinate, did not yield satisfactory results; 0·7467 gram of the salt dried at 155° gave 0·5547 gram $BaSO_4$, Ba = 43·68 per cent.; theory for the anhydrous salt requires 44·05 per cent.

The experiments described show that by the action of sodium propoxide on a mixture of hydrogen propylic maleate and propylic alcohol, maleïc acid combines with the elements of the alcohol and forms propoxysuccinic acid.

Experiments were next made on the preparation of the same acid from fumaric acid. Propylic fumarate, which does not seem to have been prepared before, is readily obtained by heating the acid with propylic alcohol and sulphuric acid on the water bath; the solution is poured into water, and the oil which separates having been washed with solution of sodium carbonate and with water, and dried with calcium chloride, is distilled. A mixture containing 124 grams of fumaric acid, 186 grams of propylic alcohol, and 13 grams of concentrated sulphuric acid gave 120 grams of the ethereal salt having the boiling point 243—245°. In preliminary experiments in which propylic fumarate was added to an equal weight of propylic alcohol in which sodium had been previously dissolved in the proportion of one-fifth atom of sodium to 1 mol. of the ethereal salt, it was found that the alkalinity of the solution quickly disappeared, and that only a very small quantity of the propoxysuccinic acid was formed; but when propylic alcohol was used which had been previously thoroughly dehydrated by distillation first from barium oxide, and then from sodium, the reaction proceeded satisfactorily. A very small amount of sodium, about one-tenth of an atomic proportion, sufficed in these circumstances to bring about the addition of the alcohol to the fumarate, and the calcium propoxysuccinate obtained from the product of the reaction amounted to about 75 per cent. of the theoretical yield. Fifty grams of propylic alcohol, in which 1·23 grams of sodium had been dissolved, were added slowly to 107 grams of propylic fumarate diluted with 57 grams of the alcohol. The mixture became nearly solid from the precipitation of a white amorphous substance which in the course of a few hours dissolved, leaving a clear red alkaline liquid, which was heated for a short time on a water bath, and then poured into water. An oil separated, a small portion of which was dried with calcium chloride and distilled in a vacuum. It boiled at 235—238° at a pressure of about 60 mm., but as analysis showed that the substance was not pure propylpropoxysuccinate, the main portion of the oil was returned to the aqueous solution from which it was obtained, and hydrolysed by heating with an excess of sodium hydroxide. The solution was made strongly acid with hydrochloric acid, which precipitated 13 grams of unaltered fumaric acid; on boiling the filtered liquid, after it had been neutralised and some calcium chloride added to it, calcium propoxysuccinate was precipitated. An estimation of calcium in the salt, dried at 100°, gave 18·49 per cent., the calculated percentage being 18·69. This salt, like the corresponding methoxy- and ethoxysuccinate, is very insoluble in water, when once it has been precipitated in the anhydrous state as described. A determination of its solubility in water at 17° showed that 100 parts of water dissolved only 0·29 gram of the salt. The acid was obtained from the calcium salt by treating it with the calculated quantity of sulphuric acid; to purify it, it was converted into lead salt, and recovered from this by the action of sulphuretted hydrogen. It crystallised similarly to the acid obtained from maleïc anhydride, but like the latter it was not obtained in the pure state, the carbon being found by analysis about 1 per cent. too low. An estimation of lead, however, in the lead salt gave correct results:—I. 0·6401 gave 0·3763 PbO; II. 0·7980 gave 0·4690 PbO. Found, I. 54·56 per cent. II. 54·55 per cent. Calculated for $C_7H_{10}O_5Pb$, 54·33 per cent. The air-dried salt is anhydrous; the quantities used for analysis lost only a few milligrams in weight when heated to 150°. The barium salt resembled that obtained from the acid from maleïc anhydride, both in general appearance and as regards the temperature at which it lost its water of crystallisation. 0·5300 of the salt, dried at 150°, gave 0·3950 $BaSO_4$; Ba = 43·82 per cent.; calculated for $C_7H_{10}O_5Ba$, 44·05 per cent.

The propoxysuccinic acid was used without further purification for experiments on the resolution of the compound into its active components by fractional crystallisation of the strychnine salt.

Resolution of Propoxysuccinic Acid.

Experiment I.—An attempt was first made to apply the method which had proved successful in the case of the methoxysuccinic acid, that is to say, to separate first the lævogyrate component as acid salt, and then the dextrogyrate component as normal salt. An aqueous solution, containing 4·36 grams of the acid, obtained from maleïc anhydride, was saturated with strychnine; the solution deposited normal salt in the form of radiating needles. These were re-dissolved by heating and another portion of 4·36 grams of the acid was added, but the solution could not be made to crystallise. A similar experiment made in alcoholic solution was not more promising. As it was apparently necessary to resort to the normal salts, strychnine was added to the above-mentioned aqueous solution until no more of the alkaloïd dissolved; the solution on standing gave 22 grams of a crystalline deposit, not of radiating needles, as was expected, but of large, transparent, flat plates. After being recrystallized twice, the crop, which now weighed 10 grams, was dissolved in water and decomposed with ammonia. The ammoniacal filtrate having been evaporated to a small bulk to remove strychnine as far as possible, was made up to 20 c.c., and then gave a rotation of —43′ in a 200 mm. tube. As the rotation of the other alkyloxysuccinic acids already investigated is in the same sense as that of their salts, it appeared that of the two normal strychnine salts of propoxysuccinic acid, that of the lævo-acid is least soluble. The separation, however, judging from the small rotation observed, had been very imperfect, and this was confirmed by our examination of the mother liquors, from which we did not succeed in isolating any active acid.

Experiment II.—We have stated under Experiment I that a neutral solution of strychnine propoxysuccinate gave a crop of radiating needles, but the solution having been warmed until the crystals were dissolved, it deposited, on cooling, a crop of plates. On repeating the experiment on the normal salt of the acid obtained from maleïc anhydride, the strychnine salt which separated first from the solution, consisted in some cases of bundles of radiating needles, in other cases of the plates referred to, and sometimes of a mixture of the two, which we could not separate by fractional crystallisation. We afterwards found that the needles and plates were really different crystalline forms of the same substance, namely the normal salt of the lævo-acid. The salt, after recrystallisation, was converted into calcium salt by methods already described. This salt was freed from colouring matter, traces of strychnine, and from inactive racemoïd salt, by methods already mentioned under the resolution of methoxysuccinic acid; when dried at 100°, it contained 18·71 per cent. of calcium, the calculated percentage being 18·69, and a determination of its solubility in water at about 17° gave the result 3·44 : 100, so that it is nearly twelve times more soluble than the corresponding inactive salt. A determination of specific rotation gave the following result: $c = 3{\cdot}3095$, $l = 2$, $\alpha = -0{\cdot}89°$, hence $[\alpha]_D = -13{\cdot}55°$. From the remaining calcium salt, a small quantity of acid was prepared, which solidified on standing and in an aqueous solution measuring 10 c.c. showed a rotation of −2·15° in a 200 mm. tube.

The mother liquor from which the normal strychnine salt of the lævo-acid had been deposited was decomposed with ammonia solution, and by the methods already described a small quantity of a dextrogyrate calcium salt was obtained which showed the following specific rotation: $c = 2{\cdot}039$; $l = 2$; $\alpha = +0{\cdot}56°$, hence $[\alpha]_D = +13{\cdot}7°$.

Experiment III.—It has been mentioned above that we did not succeed in getting the acid strychnine propoxysuccinate to crystallise in the case of the acid from maleïc anhydride. On repeating the experiment with the acid from propylic fumarate, the acid salt of the lævogyrate component was deposited from aqueous solution in the form of groups of radiating needles. Its composition was determined by precipitating 13·2 grams of the salt with ammonia solution, 8·1 grams of the dry strychnine being obtained instead of the calculated quantity, 8·6 grams. We have no reason, however, to conclude that the propoxysuccinic acids from maleïc and fumaric acids are not identical. The difference of behaviour just mentioned was probably due to some difference in the conditions of crystallisation. The mother liquor, which contained the acid salt of the dextrorotatory component, when evaporated to a small volume left a syrup which did not crystallise on standing, but on neutralizing with strychnine, the corresponding normal salt was deposited in the form of long, interlocking needles. Solutions of the ammonium salt obtained from the two strychnine salts gave the polarimetric readings −4·25° and + 1·58° respectively. As the method indicated gave both active acids in the form of crystallisable salts, one of which at all events could be easily obtained in the pure state, it was adopted for an experiment on a larger scale.

Sixty grams of strychnine were dissolved in 150 c.c. of a warm aqueous solution containing 33 grams of propoxysuccinic acid from propylic fumarate. On cooling, the solution became a nearly solid mass of radiating needles. The deposit, after being recrystallised five times, was decomposed with ammonia, and gave 28 grams of strychnine equivalent to about 14 grams of acid or 84 per cent. of the maximum possible yield. The main mother liquor was mixed with the mother liquors from the three first recrystallisations; the solution, when saturated with strychnine, gave a deposit of normal dextro-salt, which after two crystallisations weighed 46 grams somewhat moist. The strychnine salts were converted into calcium salts with the precautions to insure purity previously mentioned. An estimation of calcium in the lævo-salt gave 18·70 instead of the calculated 18 69 per cent. The specific rotations of the two salts at 12° were as follows: $c = 2{\cdot}6030$, $l = 2{\cdot}2$, $\alpha = -0{\cdot}83°$, hence $[\alpha]_D = -14{\cdot}49°$; $c = 1{\cdot}9394$, $l = 2$, $\alpha = 0{\cdot}55°$, hence $[\alpha]_D = +14{\cdot}18$. The concentration was deduced from the specific gravities of the solutions and their percentage composition by weight, the latter being found by evaporating known weights of the solutions to dryness. The active acids were obtained from their respective calcium salts as described in the case of the methoxysuccinic acids. They were left as syrups on the evaporation of their aqueous or ethereal solutions, which solidified slowly. The substances were very hygroscopic, and did not give sharp melting points. The lævo-acid melted at about 67°, and the dextro-acid at 63—66°. The melting point of the active acids is apparently lower than that of the racemoïd form, the melting point of which, in the case of the acid from maleïc anhydride, was found to be 73—75°. The lævo-acid being dried in a vacuum gave the following results on combustion.

0·4436 gave 0·7764 CO_2 and 0·2722 H_2O. C = 47·73; H = 6·82.

$C_7H_{12}O_5$ requires C = 47·73; H = 6·82 per cent., numbers identical with those found.

Our experiments show that propoxysuccinic acid can be resolved into its active components by fractional crystallisation of the strychnine salts in two different ways; first by means of the normal salts when the salt of the lævogyrate acid crystallises first from the solution in the form of bundles of radiating needles or rectangular plates; second by means of the acid salts, when the salt of the lævogyrate acid crystallises first, the corresponding salt of the dextrogyrate acid being either a syrup, or crystallising with difficulty; the dextrogyrate acid is afterwards separated from the solution as the normal salt. With respect to the dimorphous normal salt of the lævogyrate acid, we found that the air-dried plates melted at 112—113°, but after being dried at 100° they underwent a change independent of loss of water of crystallisation, and then melted at 108—109°. The needles sintered at 82°, became solid again at a higher temperature, and melted at 104°; on drying them, however, for some time at 100°, they assumed a prismatic form and then melted at the same temperature as the dried plates, namely 109°.

On observing under the microscope the crystallisation of a specimen of the salt, which had been prepared from pure lævogyrate acid, we found that it crystallised at first in fine needles and prisms, but that by friction the liquid quickly solidified to a mass of rectangular plates.

Specific rotations of both active acids in aqueous solution, and of the lævo-acid in acetone were determined as given below. The solutions were made by dissolving weighed quantities of the acids dried in a vacuum and making the liquids up to known volumes. The more dilute aqueous and acetone solutions were obtained by the dilution of aliquot parts of the more concentrated solutions. The temperature was 12°.

	c.	*l.*	*α.*	$[\alpha]_D$.
Water	7·7600	4	−11·30°	−36·40°
,, ...	3·1040	4	− 4·50	−36·24
,, ...	7·5600	4	+10 90	+36·04
Acetone....	5·6880	1	− 3·60	−63·29
,, ...	2·2752	1	− 2·93	−64·39

Though the analysis of the inactive acids did not give good results, it appears from the analysis of the active acid quoted above, and from the fact that the oppositely active acids gave nearly identical specific rotations, that the compounds had been purified by the frequent crystallisations of the strychnine and other salts, and we think, therefore, that although the quantity of material available for experiment was small the specific rotatory powers found are nearly, if not quite, correct.

Besides the calcium salts which have been already described, the salts of potassium and barium were also examined.

Potassium Propoxysuccinates.

A solution of the hydrogen potassium salt was prepared by neutralising a measured volume of a solution of the dextro-acid, and then adding to this an equal quantity of the same acid solution. A solution of the normal salt was prepared from that of the acid salt by neutralising it completely, and the concentration was found by evaporating 20 c.c., and converting the residue into sulphate. This residue dried at 100° was found to contain 31·05 per cent. of potassium. Calculated K = 31·01 per cent. The specific rotatory powers of the salts were then determined.

Acid Salt.—$t = 18°$, $l = 4$, $c = 3·8152°$, $\alpha = +4·93°$, $[\alpha]_D = +$ 32·30.

Normal Salt.—I. $t = 18°$, $l = 4$, $c = 3·665°$, $\alpha = +2·53°$, $[\alpha]_D = + 17·26°$.

II. $t = 18°$, $l = 4$, $c = 1·8325$, $\alpha = +1·37°$, $[\alpha]_D = +18·69°$.

Barium Propoxysuccinate.

It was prepared by neutralising a solution of the lævo-acid with barium hydroxide; on evaporating the solution, the salt was deposited in the form of crystalline scales, which, after being dried at 150°, were found to contain 43·83 per cent. of barium, the calculated percentage being 44·05. The specific rotatory power of the anhydrous salt was determined as follows.

I. $t = 18°$, $l = 4$, $c = 3·649°$, $\alpha = -1·46°$, $[\alpha]_D = -10·00°$.
II. $t = 18°$, $l = 4$, $c = 1·4596$, $\alpha = -0·61°$, $[\alpha]_D = -10·45°$.

The results of our observations on the activity of propoxysuccinic acid and its salts were exactly such as might have been anticipated from the relation of the acid to methoxy- and ethoxy-succinic acids. The specific rotatory power of the acid in aqueous solution, as in the case of its homologues, is independent of concentration, as far as our observations go, and in acetone it shows a very large increase. The propoxysuccinates examined are active in the same sense and to a less extent than the acids from which they are derived, the normal potassium salt being less active than the corresponding acid salt, and the specific rotatory power of the normal salts increases with dilution. It was found in the case of methoxy- and ethoxy-succinic acids that increase of the oxyalkyl group caused an increase of activity in the free acids, and a corresponding change in the activity of the salts at similar concentrations. Thus calcium *d*-methoxysuccinate is lævorotatory, but becomes less so in dilute solution; whilst calcium *d*-ethoxysuccinate is dextro-rotatory, and becomes more so on dilution. Barium *d*-methoxysuccinate is lævorotatory, but becomes dextrorotatory in very dilute solution, whilst the corresponding ethoxysuccinate shows lævorotation only in very concentrated solutions, these relations being explained by the dextrorotatory effect produced by increasing the oxyalkyl group, and by dissociation on dilution. It was to be expected that propoxysuccinic acid would be more active than ethoxysuccinic acid, that the calcium, barium, and potassium dextropropoxysuccinates would be to a greater extent dextrorotatory than the corresponding ethoxysuccinates, and that the normal potassium salt being more dissociated than the barium and calcium salts, would give a higher rotation. These anticipations are all realised.

The theoretical bearing of the observations which have been described will be discussed in the following paper.

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XCVII.—*Ethereal Salts of Active Methoxy- and Ethoxysuccinic Acids.*

By THOMAS PURDIE, F.R.S., and SIDNEY WILLIAMSON, Ph.D.

THE following research was undertaken as a contribution towards the solution of the problems relating to optical activity which have been raised by the well-known theory of Guye, its immediate object being the preparation and examination of some of the ethereal salts of the active alkyloxysuccinic acids. The ingenious theory referred to has already done excellent service as an incentive to the preparation and study of a number of series of optically active substances, and in the case of some of these series, it has undoubtedly received striking support. In various instances, on the other hand, the theory in its present form does not accord with the facts which have been brought to light, and it is already evident that many more active compounds of simply related constitution must be studied before it can be decided that any general expression can be found for the quantitative relation of optical activity to chemical composition.

The series of ethereal salts which have been hitherto chiefly examined, such as those of the acidyltartaric and glyceric acids, besides the variable alkylcarboxyl groups, possess also a variable acidyl group, and quite recently some halogen derivatives have been studied, but so far no ethereal salts of etheric acids have been investigated. These compounds are of a somewhat simpler constitution than the acidyl derivatives referred to, and present the peculiarity of a variable etheric alkyl radicle, which we have already shown exerts a remarkable influence on activity in the case of the alkyloxysuccinic acids. The fact that no active ethereal salts of this description have yet been studied is accounted for, no doubt, by the difficulty of obtaining them; the difficulties attending their preparation from the naturally occurring optically active hydroxy acids have not yet been overcome, and their preparation from other sources involves the tedious process of the resolution of a racemoïd acid into its active components.

The most obvious method for the preparation of the active ethereal alkyloxysuccinates is the replacement of the hydroxylic hydrogen of ordinary ethereal malates by alkyl groups, either by the action of sodium, and subsequent treatment of the sodium derivative with an alkyl iodide, or by conversion into the active monohalogen-succinates, and subsequent treatment of these with sodium alkyloxide. We have not succeeded in preparing the compounds in question by either of these processes. Andreoni has described (*Ber.*, 1880, **13**, 1394) the preparation of a diethylic ethoxysuccinate from ethylic malate by the first of the two methods referred to, but no analysis of the compound is given, and its optical activity was apparently not tested. We found, on repeating his experiments, that the sodium derivative of ethylic malate did not react with ethylic iodide at the temperature of the water bath; on heating at 150° in a sealed tube, sodium iodide was formed, but we failed to obtain the compound in question from the product of the reaction. A similar experiment in which methylic iodide was heated with the sodium derivative of methylic malate was equally unsuccessful. In trying the second process above referred to, we prepared methylic chlorosuccinate from methylic malate by the method since described by Walden (*Ber.*, 1895, **28**, 1290); it was strongly dextrorotatory. On adding an alcoholic solution of sodium methoxide, the reaction proceeded spontaneously with precipitation of sodium chloride, but methylic fumarate which crystallised from the filtered solution in large quantity was the chief, if not the only, product of the reaction.

It seemed possible that the acetyl group might be more readily replaced by an alkyl radicle than the halogen atom. We accordingly prepared methylic acetylmalate by the method of Anschutz (*Ber.*, 1885, **18**, 1952). The liquid, when redistilled, boiled mostly at 152—153° at 28 mm., and gave the rotation −26·97° at 18° in a 100 mm. tube. The specimen did not contain very much methylic fumarate, as the pure substance described recently by Anschütz (*Zeit physikal. Chem.*, 1895, **16**, 495) gives the rotation −27·398° under similar conditions. The acetylmalate (1 mol.) diluted with methylic alcohol was treated with alcoholic solution of sodium methoxide (1 mol.), the latter being added very slowly to the former, so as to prevent rise of temperature. Silky crystals, apparently of sodium acetate, were formed at once, and the product smelt of methylic acetate. The alcohol was distilled from the liquid after it had stood for 12 hours, and the residue, which was semi-solid, was treated with a little water. By extraction with ether, and subsequent evaporation of the latter, an oil was obtained, from which a small quantity of methylic fumarate crystallised. An alcoholic solution of the oil was optically inactive. By hydrolysing a part of it with barium hydroxide, a soluble barium salt was obtained, which, when dried at 150°, was found on analysis to contain 47·83 per cent. of barium. Another part of the oil was hydrolysed with potassium hydroxide; the solution, after being neutralised, gave, on addition of calcium chloride and boiling, an insoluble calcium salt, which was found to contain 21·50 per cent. of calcium. As the calculated percentages for barium and calcium methoxysuccinates are respectively 48·41 and 21·51, it was evident that the oil was inactive methylic methoxysuccinate. On cooling it, and adding to it a crystal of this substance, it solidified to a crystalline mass, the melting point of which was found to be identical with that of the ethereal salt mentioned, namely, 28°. In another similarly conducted experiment, an alcoholic solution of the oil showed a slight rotation of $-15'$ ($l = 200$ mm.), but this was probably due to traces of unaltered acetylmalate. In the aqueous solution from which the oil was extracted, no acid, except acetic acid, was detected. It appears, therefore, that the chief product of the action of alcoholic sodium methoxide on methylic acetylmalate is inactive methylic methoxysuccinate; the first product is doubtless methylic fumarate, which is then converted into the substance in question by the addition of the elements of alcohol in the presence of small quantities of sodium methoxide.

Having failed to procure the ethereal alkyloxysuccinates from the malates, we had to resort to their preparation from the active alkyloxysuccinic acids obtained by the resolution of the racemoid acids which are formed by the addition of the elements of alcohols to fumaric acid. Owing to the tedious nature of these processes, and the difficulty of obtaining a sufficient supply of material, we have been compelled to confine ourselves for the present to methoxy- and ethoxy-succinic acids. In what follows, we describe the methods by which the active acids were obtained from the racemoïd compounds, and the preparation of the active methylic, ethylic, propylic, and butylic salts. The specific rotations of these compounds were determined. We took the opportunity of making some observations of the activity of some of the strychnine salts, and also of that of ethoxysuccinic acid in organic solvents, for the purpose of comparison with similar observations made on methoxy- and propoxy-succinic acids, which are recorded in the preceding paper.

Resolution of Inactive Methoxysuccinic acid.

The method employed was the fractional crystallisation of the strychnine salts which is described in detail in the preceding paper, but with modifications suggested by our experience in resolving inactive ethoxysuccinic acid, which is recorded below. Instead of dissolving the acid and alkaloïd in molecular proportions and crystallising first the acid salt of the lævo-acid and then, after complete neutralisation of the mother liquor with strychnine, the normal salt of the dextro-acid, we found it better to take the acid and alkaloïd in the proportion of 2 mols. of the former to 3 mols. of the latter; under these conditions, crystallisation being induced by pure nuclei of the salts, the very insoluble normal lævo-salt is first deposited, the much more soluble acid dextro-salt being entirely retained in the solution. The mother liquor having ceased, after concentration, to deposit any further crops of the more insoluble salt, it is completely neutralised with strychnine, after which one or two small crops of the same salt are usually again deposited; these having been removed, and the mother liquor concentrated somewhat by evaporation, the normal dextro-salt crystallises readily. Several successive crops of the salt are removed, until it is found that the mother liquor begins again to yield some of the salt of the lævo-acid. A mixture of the salts is readily detected, as the normal lævo-salt crystallises in large, square plates, the normal dextro-salt in long, thin needles. The salts obtained in the manner described were decomposed with ammonia after being recrystallised, and the solutions of the ammonium salts converted successively into calcium salts, free acids, and finally acid potassium salts as indicated in the preceding paper. The specific rotation of the dextro-salt was +22 19° ($c = 8$, $t = 15°$), that of two successive fractions of the lævo-salt −22·87° and −23·50° ($c = 8$, $t = 6°$). The highest specific rotations found for specimens of the salt prepared by the other methods of resolution were +23·23° and −23·18°, from which it appears that the dextro-salt still contained 4 to 5 per cent. of racemoid salt.

Resolution of Inactive Ethoxysuccinic acid.

The inactive acid was prepared from ethylic fumarate by methods previously described (Trans., 1893, 63, 229). It was usually precipitated from the product of the reaction, however, not as lead but as calcium salt; the latter was found to yield a fairly pure product when decomposed with rather less than the calculated quantity of sulphuric acid, especially if the salt is first digested with alcohol to remove the colouring matter. The syrupy acid can be made to crystallise rapidly by stirring; it then forms a paste, from which it is obtained by filtration as a white, crystalline powder. When it crystallises slowly, it forms large, transparent crystals.

Before describing the process actually used for resolving the inactive acid into its active components, we may mention some unsuccessful attempts we made to resolve it by simple crystallisation. Having noticed on one occasion that the acid crystallised in a manner which differed from its usual form, we induced crystallisation by stirring the syrup with a nucleus of the dextro-rotatory isomeride, and repeated the process on the fraction of crystallised acid thus obtained; the product, however, was quite inactive. Similar attempts with the hydrogen ammonium salt, the active forms of which are readily recognisable, were also unsuccessful. The crystallisation of the zinc salt, which forms a syrup on evaporating its aqueous solution. seemed to be induced by a crystal of active salt, but the salt which crystallised was inactive.

It has been shown in a previous communication (*loc. cit.*) that the dextro-rotatory form of this acid can be obtained by the action of *Penicillium glaucum* on the racemoïd compound; the method, however, is not suitable for obtaining the substance on a large scale, and we had recourse therefore to the method of resolution by means of salts of the alkaloïds. Experiments already described showed that among several alkaloïds which were tried cinchonidine was the only one which gave the desired result. Our later experience with the other alkyloxysuccinic acids led us to conclude that strychnine would probably answer the purpose better, and we found that a very effective separation of the active forms could be attained by means of this alkaloïd.

Preliminary experiments showed that when the acid and strychnine were dissolved in water in proportion to form the normal salts of both acids, the salt of the dextro-acid was deposited first. Thus, from 10 grams of inactive acid, 20 grams of recrystallised normal dextro-salt were obtained, the active acid from which, when concentrated to 15 c.c. in aqueous solution, gave a rotation of +11·2° in a 200 mm. tube. When the acid and alkaloïd were dissolved in proportion to form the acid salt of both acids, the acid salt of the lævo-acid was usually first deposited. Thus, in an experiment in which 9 grams of acid were taken, the first deposit consisted of the acid lævo-salt, which, after being recrystallised and then decomposed with ammonia solution, gave 6 grams of strychnine, corresponding with about 3 grams of active acid. The aqueous solution of acid prepared from this, when concentrated to 10 c.c., gave the rotation —4·25° in a 200 mm. tube. It was found, however, on one occasion, in a later experiment on a larger scale, that, when the acid and alkaloïd were in the same proportion as in the experiment just mentioned, the normal salt of the dextro-acid crystallised first; we had reason to believe that the crystallisation was induced by the accidental introduction of a nucleus of the salt in question. From 100 grams of acid and 206 grams of strychnine, a crop of the normal dextro-salt was thus obtained, which, after being recrystallised twice, weighed 92 grams, corresponding with about 18 grams of dextro-acid. The active acid prepared from this salt was pure. 55 grams of the acid lævo-salt were then deposited, corresponding with about 18 grams of lævo-acid, from which the pure acid ammonium lævo-salt was afterwards obtained. The composition of these salts was determined by precipitating and weighing the strychnine.

In the course of our experiments the following facts regarding the general appearance and solubility of the strychnine salts of the active ethoxysuccinic acids were ascertained.

Normal Dextro-salt.—Rectangular plates, very sparingly soluble in water. 100 c.c. of an aqueous solution saturated at the ordinary temperature contain only about 2 grams of the salt

Normal Lævo-salt—Bundles of long, slender needles of satiny lustre, more soluble than the preceding salt.

Acid Dextro-salt.—Very soluble: crystallises with some difficulty from very concentrated solutions as a fine powder, consisting of short, microscopic prisms.

Acid Lævo-salt.—Crystallises readily in small groups of radiating, soft, silky needles, much less soluble than the preceding salt, much more soluble than the normal dextro-salt, and apparently somewhat more soluble than the normal lævo-salt.

In our experiments on a larger scale, three different methods of separation, based on the facts relating to solubility just quoted, were practised; they may be summarised as follows.

First Method.—Acid and strychnine were dissolved in equal molecular proportions so as to form the acid salts. By means of a nucleus of the normal dextro-salt a deposit of this salt was obtained, followed by a deposit of the acid lævo-salt. The amount of strychnine, calculated from the weight of the two salts removed from the solution, which was required to form the normal salt of the dextro-acid and the acid salt of the lævo-acid still present in the solution, was now added, which caused the deposition of another crop of the normal dextro-salt, followed by two crops of the acid lævo-salt. The mother liquor was then saturated with strychnine; after removing another small crop of the normal dextro-salt, three crops of the normal lævo-salt were deposited in succession. The final mother liquor was found, by precipitation of the strychnine, to contain only about 6 grams of acid, 100 grams of acid having been originally used.

Second Method—Acid and strychnine were dissolved in equal molecular proportions; no nucleus being added, the acid lævo-salt was first deposited. The necessary quantity of strychnine was now added to form the normal salt of the dextro-acid, two crops of which then crystallised, and afterwards a crop of the lævo-salt; the mother liquor being saturated with strychnine gave a little more normal dextro-salt, and finally normal lævo-salt.

Third Method—Acid and strychnine were dissolved in the proportion of 2 mols. of the former to 3 mols. of the latter, so as to form the normal dextro-salt and the acid lævo-salt. Under these conditions the normal dextro-salt always crystallised first. Several crops of this salt having been removed, the mother liquor was saturated with strychnine, after which a little more of the same salt was deposited. On concentrating the mother liquor, successive crops of the normal lævo-salt were obtained.

We found it always advisable to sow the solutions with pure nuclei of the particular salt which was to be crystallised. In every case the crops of crystals were recrystallised until they were found to be homogeneous when examined with the microscope. It may be mentioned that crops of crystals consisting of a mixture of the normal dextro-salt with the normal or acid lævo-salt may often be purified by shaking with cold water, when the two latter salts go into solution, the hard, gritty crystals of the dextro-salt being scarcely at all dissolved. Of the three methods of separation, the last mentioned is the best. As an example of its efficiency, we may state that in one experiment in which 139 grams of acid were taken, the practically pure recrystallised normal dextro-salt obtained from the two-thirds neutralised solution weighed 255 grams when dried at 100°, corresponding to about 50 grams of active acid, or 70 per cent. of the total dextro-acid present.

Strychnine Salts of the Alkyloxysuccinic acids.

Both active forms of the three acids examined, namely, methoxy-, ethoxy-, and propoxy-succinic acids form acid and normal salts with strychnine, and the corresponding salts of the three acids show certain general resemblances. Of the four salts of each acid, the acid dextro-salt is in each case much the most soluble, the methoxy- and ethoxy-succinates crystallising with some difficulty from very concentrated solutions, and the propoxysuccinate apparently not crystallising at all. The different solubility of the acid salts can therefore be made use of for separating the active forms in the case of all three acids. Of the normal salts, the methoxy- and propoxysuccinates resemble each other; the dextro-salts crystallise in the form of long needles, and are more soluble than the lævo-salts; the lævo-salts are both dimorphic, crystallising either in the form of plates or needles, the plates being the stable form, in the case at least of the methoxy-succinate. In crystallising neutral solutions of the strychnine salts of these two acids the normal salt of the lævo-acid is therefore first deposited. In the case of the normal salts of ethoxysuccinic acid, however, it is the dextro-salt which crystallises in plates, and which is the more insoluble of the two forms.

Van't Hoff (*Die Lagerung der Atome im Raume*, p. 103) has pointed out that the rotations of the alkaline methoxy- and ethoxy-succinates in dilute solution are in conformity with the law of Oudemans, and that the ionic rotations deduced from the normal salts of the alkalis are about 15° and 23°, and of the semi-dissociated acids, deduced from the acid salts about 29° and 37° respectively. It seemed of interest to ascertain whether the salts of the alkaloids followed the same law. For this purpose we have determined the specific rotations of several of the strychnine salts and compared the results with the numbers deduced from the known ionic rotations of the acids and alkaloid. We find that the experimental results agree closely with the calculated values.

Normal Strychnine l-*Methoxysuccinate.*—The salt contains water of crystallisation. Two air-dried specimens lost each, when dried at 100°, 12·87 per cent. in weight, and dried at 120°, at which temperature the substance begins to get slightly brown, 13·01 and 13·10 per cent.; the calculated percentage for $7H_2O$ is 13·38.

The concentration of the solution which was used for the following determination of specific rotation was found by evaporating 20 c.c. of a saturated solution and drying the residue at 110°.

$$t = 12°;\ l = 4;\ c = 3·7065;\ \alpha = -4·4°, \text{ hence } [\alpha]_D = -29·68°.$$

Hädrich (*Zeit. physikal. Chem.*, 1893, **12**, 483) found the molecular rotation of the salts of strychnine in dilute solution to be −113°, which gives −33·73° for the specific rotation of the strychnine ion. The specific rotation of the acid ion calculated from the mean of that of the normal ammonium and potassium salts (Trans., 1893, **63**, 239) is 14·86°. The molecular weights of the ions of the alkaloid and acid being 335 and 146 respectively, then supposing the dissociation of the salts to be complete, its specific rotation should be $-\dfrac{670 \times 33·73 + 146 \times 14·86}{816} = -30·35°$, a number which agrees as closely as could be expected with the experimental value 29·68°. It should be stated that in dissolving the salt, it suffers a certain amount of hydrolysis, a little strychnine being always left undissolved which would account for the value found by experiment being low.

From the specific rotations of the valerates of inactive organic bases, Guye and Rossi (*Bull. Soc. Chim.*, 1895, [3], **13**, 464) have seen reason to conclude that these salts undergo hydrolytic dissociation in water, and that electrolytic dissociation has only a subordinate influence on the rotations. It is extremely improbable that hydrolytic dissociation is the explanation of the case above referred to, and it may be pointed out that the specific rotation of strychnine methoxysuccinate calculated from that of the acid in water, instead of from that of the ion, amounts to 33·7° and does not agree, therefore, so closely with the observed result.

Acid Strychnine l-*Ethoxysuccinate.*—Dried in a vacuum or at 100°, it lost 6·61 per cent. of water; the calculated percentage for $2H_2O$ is 6·77. At 100° it fuses and solidifies on cooling to a hard, horny mass; 55 grams of the dry salt gave, on precipitation with ammonia, 36 grams of strychnine, the calculated weight being 37 grams.

The specific rotation was determined at three different concentrations. The most concentrated solution was prepared by dissolving a known weight of the dry salt in water and diluting the solution to a measured volume; the other solutions were prepared from this by suitable dilution.

I. $t = 11°$; $l = 4$; $c = 7{\cdot}614$; $\alpha = -9\;88°$, $[\alpha]_D = -32{\cdot}44°$.
II. $t = 11°$; $l = 4$, $c = 3{\cdot}0456$; $\alpha = -4{\cdot}15°$, $[\alpha]_D = -34{\cdot}07°$.
III. $t = 11°$; $l = 4$; $c = 1{\cdot}2182$; $\alpha = -1{\cdot}70°$, $[\alpha]_D = -34\;89°$

The rotation increases with dilution. The rotation of the acid ion, calculated from the acid ammonium salt, is $-36\;07°$; the calculated specific rotation is therefore

$$-\frac{161 \times 36\;07 + 335 \times 33{\cdot}73}{496} = -34\;49°,$$

which agrees closely with that found for the salt in dilute solution.

Normal Strychnine d-*Ethoxysuccinate.*—Estimations of water of crystallisation by drying in a vacuum gave the numbers 11·18, 11·27 per cent.; the calculated percentage for $6H_2O$ is 11 51. The substance does not lose further in weight when heated to 105°. The composition of the salt was determined by weighing the strychnine precipitated by ammonia; 53·31 grams of dry salt gave 42·71 grams of dry strychnine, the calculated quantity being 42·9 grams.

The following observation of the activity of the salt was made on a saturated aqueous solution prepared at the ordinary temperature so as to avoid decomposition of the salt as far as possible, and its concentration was estimated by evaporating a known volume of it to dryness.

$t = 11°$; $l = 4$; $c = 2{\cdot}1275$; $\alpha = -1{\cdot}9°$, hence $[\alpha]_D = -22{\cdot}33°$.

The acid ionic rotation deduced from the rotation of the normal ammonium salt (*loc. cit.*) is $+22{\cdot}41°$, hence the calculated specific rotation of the strychnine salt is

$$\frac{160 \times 22{\cdot}41 - 670 \times 33{\cdot}73}{830} = -22\;91°.$$

Normal Strychnine l-*Ethoxysuccinate.*—The air-dried salt lost 7·83 per cent. of water when dried at 100°; the calculated percentage for $4H_2O$ is 7·98. At 110° it fuses and becomes brown. Determinations of the specific rotation of the salt gave the following results:—

I. $t = 17°$; $l = 4$; $c = 7{\cdot}828$; $\alpha = -9\;25°$; $[\alpha]_D = -29{\cdot}54°$.
II. $t = 17°$; $l = 4$; $c = 3{\cdot}131$; $\alpha = -3{\cdot}96°$; $[\alpha]_D = -31{\cdot}62°$.
III. $t = 17°$; $l = 4$; $c = 1{\cdot}252$; $\alpha = -1{\cdot}7°$; $[\alpha]_D = -33\;95°$.

The calculated value is $\frac{160 \times 22{\cdot}41 + 670 \times 33{\cdot}73}{830} = -31{\cdot}55°$.

The agreement between the experimental and calculated values is not so close in the last case, but the results on the whole show that in dilute solutions of strychnine methoxy- and ethoxy-succinates the acid and alkaloïd retain the activity which they exhibit when combined with alkalis and mineral acids respectively.

Active Hydrogen Ammonium Ethoxysuccinates.

The recrystallised strychnine salts were decomposed with ammonia, and the filtered ammoniacal solutions having been evaporated to a small bulk to precipitate traces of strychnine, were treated in one of two ways; in some cases the calcium salt was prepared, and this, after digestion with alcohol to remove traces of strychnine, was converted into acid by methods already described, and in the event of the latter being coloured, finally into acid ammonium salt, which crystallises well; in other cases the solutions in question were treated with animal charcoal, which effectually removed not only the colouring matter, but also traces of strychnine, and were then repeatedly evaporated on the water bath until the normal ammonium salt was converted into the acid salt. The latter was then obtained in the pure state by crystallisation, the presence of any inactive salt being readily detected by its distinct form.

Both active salts were found to crystallise in the same form as the dextro-salt obtained by the action of *Penicillium*, and their activity was also practically identical with that of the latter at similar concentrations. The following determinations of specific rotations of different preparations of the salts may be quoted. The solutions were prepared by dissolving weighed quantities of the air-dried hydrated salts and making the solutions up to known volumes; the specific rotations are calculated on the hydrated salts which, according to former analyses, contain 1 mol. H_2O.

t.	*c.*	*l.*	*a.*	$[\alpha]_D$.
17°	18·7500	2	+10·35°	+27·60°
—	10·0300	,,	+ 5·71	+28·46
19	7·5752	,,	+ 4·35	+28·71
21	10·3680	,,	− 5·88	−28·36
—	10·0273	,,	− 5·70	−28·42
11	4·9000	4	− 5·78	−29·49

The specific rotation rises slightly with dilution; this is shown with most certainty in the first and third determinations, 27·6 and 28·71, which were made on the same specimen of salt.

Dr. Hugh Marshall, who kindly undertook the crystallographic examination of the two active salts, has furnished us with the following report:—

Active (d- *or* l-) *Hydrogen Ammonium Ethoxysuccinate.*

System :—Rhombic, bisphenoidal class.

$$a : b : c = 0\ 7877 : 1 : 1{\cdot}3764.$$

Forms observed :

$$c = \{001\},\ q = \{011\},\ q'\ \{012\},\ r = \{101\}.$$

Cleavage {010}, perfect.

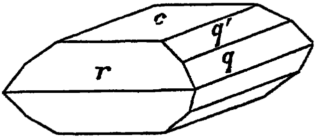


Table of Angles.

Angle.	n.	Measured		Mean.	Calculated.
001 011	16	53° 53′	54° 8′	54° 0′	—
001 : 101	16	60 10	60 24	60 13	—
001 : 012	7	34 28	34 56	34 39	34° 32′
101 . 011	11	72 51	73 4	73 0	73 1·5
101 012	2	65 51	65 59	65 55	65 51

The two salts have exactly the same appearance, as sphenoidal forms are absent, and cannot be distinguished by inspection. The crystals are large, clear, and colourless. They are sometimes prismatic along the brachy-diagonal, but generally they are tabular on the face *c*. In some of the smaller crystals, the faces of the form {012} are small or entirely wanting, but in the larger ones they almost equal those of the form {011}. The faces of these two forms are sometimes striated longitudinally, but as a rule the faces are good and give excellent reflections.

Examined in convergent polarised light, a cleavage plate shows the interference figures of a rhombic crystal with strong double refraction, negative. The axes lie in the plane 001, and have an apparent angle of about 20°, $\rho < \nu$.

Active Ethoxysuccinic acids.

The active acids crystallised similarly to the dextro-acid obtained by the action of *Penicillium*. They were extremely hygroscopic, and their melting point (76—80°) was not sharp. An analysis of the dextro-acid dried in a vacuum gave the following results : C = 44·52, H = 6·33. Calculated for $C_6H_{10}O_5$: C = 44·44 ; H = 6 17 per cent.

The specific rotation of the acids in aqueous solution was somewhat higher (0·5° to 1°) than that of the acid obtained by the fermentation method. We give below the results obtained on several different preparations, covering a greater range of concentration than was possible in previous observations, and also our observations on the activity of the substances in organic solvents. The acids were dried in a vacuum till constant. The acid used in these observations was the dextro-acid, except in the case of acetone. Of the specific rotations in water, those bracketed were made on the same preparation.

	t.	*l.*	*c.*	*a.*	$[\alpha]_D$.
Water.................	17°	2	22·5865	+15·69°	+34·73° ⎫
"	17	2	13·4260	+ 9·24	+34·41 ⎭
"	12	2	8·1000	+ 5·59	+34·51 ⎫
"	12	4	1·6200	+ 2·25	+34·72 ⎭
Chloroform..	12	2	11·6125	+11·09	+47·75
"	12	2	4·7966	+ 4·37	+45·55
"	11	2	4·5166	+ 3·99	+44·17
"	11	2	1·5989	+ 1·26	+39·40
Ethylic alcohol	11	2	11·8130	+14·31	+60·57
Acetone.................	14	4	9·5664	−21·45	−63·39
"	14	4	3·8266	− 9·93	−64·87
"	14	4	1·5306	− 4·07	−66·48
Ethylic acetate	18	2	19·9675	+28·07	+70·29
"	18	2	11·5025	+16·09	+69·94
"	18	2	10·0580	+14·18	+70·49
"	18	2	5·3530	+ 7·55	+70·52

Ethereal Salts of Methoxy- and Ethoxy-succinic acids.

It has been shown in previous papers that when the product of the action of small quantities of sodium alkyloxide on mixtures of fumaric ethers and alcohols is added to water, the normal ethereal salt of the alkyloxysuccinic acid separates from the solution as an oil. Methylic methoxysuccinate has been already described (Trans., 1891, **59**, 469). Some of the corresponding ethylic compound was isolated on the occasion of two of our preparations of ethoxysuccinic acid. After being dried with calcium chloride and fractionated, one specimen boiled at 163—164° at 70 mm., the other at 148—150° at 40 mm.; the specific gravities were respectively *d* 17·5°/4° = 1·0400 and *d* 17°/4° = 1·0403. As the percentage composition of the compound differs but slightly from that of ethylic fumarate, and its purity could not therefore be tested by ordinary analysis, we hydrolysed weighed quantities of each specimen with a measured volume of standard alkali, and estimated the excess of alkali with standard acid. I. 100 parts required 37·1 parts of NaOH. II. 100 parts required 51·6 parts of KOH. The calculated quantities of NaOH and KOH respectively are 36·7 and 51·5 parts.

With the view of finding the most productive method of preparing the active ethereal salts from their acids, some experiments were made first with the inactive acid. As the use of hydrochloric or sulphuric acid as etherifying agents had to be avoided on account of the risk of decomposing the acids or of causing racemisation, the only available methods were heating the acid and alcohol together in a sealed tube, and acting on the silver salt with an alkyl iodide. A solution of 15 grams of dry inactive ethoxysuccinic acid in 30 grams of ethylic alcohol was heated in a sealed tube for eight hours at 175—185°. An oil remained after evaporating the alcohol from the product of the reaction, which, after being washed with dilute sodium carbonate solution, and then with water, and dried with anhydrous sodium sulphate, boiled at 125° at 12 mm. 100 parts of the ethereal salt required the calculated quantity of sodium hydroxide, namely 36 7 parts, for hydrolysis, and its specific gravity was *d* 15°/4° = 1·0391. The substance was therefore pure ethylic ethoxysuccinate, but as the product amounted to only about 43 per cent. of the theoretical yield, the method was not adopted.

To test the second method, silver ethoxysuccinate was prepared by adding silver nitrate to a neutral solution of the ammonium salt. It was deposited as a slimy, sparingly soluble precipitate, which was difficult to wash, and had to be ground up repeatedly in a mortar with water till it formed a thin paste. The salt darkened slightly when exposed to light, but was dried at 100° without decomposition. The finely powdered substance was added slowly to an excess of methylic iodide. The action was slow at first, but became rapid as the temperature rose. The mixture having been heated for a short time on the water bath under a reflux condenser, was diluted with anhydrous ether and filtered. The oil which remained after evaporating the excess of methylic iodide and the ether boiled entirely at 114° at 14 mm. Its specific gravity was *d* 15°/4° = 1·1054: 100 parts required 42·08 parts NaOH for hydrolysis, the calculated quantity for methylic ethoxysuccinate being 42·1 parts.

As the action of the alkyl iodide on the silver salt proceeded very readily and seemed to be complete, the method was adopted for the preparation of the active ethereal salts. The silver salts of the active acids were found to be very slightly soluble, like that of the inactive acids, and they were similarly prepared, partly from the acid and partly from the acid potassium salt in the case of methoxysuccinic acid, from the acid and acid ammonium salt in the case of ethoxysuccinic acid. The acids and salts used were those whose specific rotation has been quoted. The silver *d*-methoxysuccinate was found to contain 59 23, and the *l*-methoxysuccinate 59·27 per cent. of silver; $C_5H_6O_5Ag_2$ requires 59·67 per cent.

The silver ethoxysuccinates were precipitated in the form of small fine needles. The dextro-salt gave on analysis 57·51, and the lævo-salt 57·13 per cent. of silver; $C_6H_8O_5Ag_2$ requires 57·45 per cent. The dried silver salt amounted to about 88 per cent. of the theoretical yield.

The active ethereal salts were obtained from the silver salts in the manner described above. The following details may be added. About twice the calculated quantity of alkyl iodide was taken. In the case of the ethereal salts of higher molecular weight, the reactions proceeded very vigorously owing to the higher temperature attained. The product was always distilled under reduced pressure. In almost every case as soon as the ether and alkyl iodide had evaporated, the thermometer rose rapidly to the boiling point of the ethereal salt, which distilled within a range of one or two degrees, a few drops only of higher boiling liquid being finally left in the distilling flask. The weight of ethereal salt obtained amounted to 80 or 90 per cent. of the theoretical yield calculated on the silver salt used. The liquids after the first distillation usually still contained traces of alkyl iodide, in consequence of which they became slightly coloured on standing. Their activity having been observed, they were distilled again, about 1 c.c. being allowed to pass over before the main fraction was collected and a similar residue left in the distilling flask; the process was repeated until a product of nearly constant specific rotation was obtained. The specific gravity in each case was taken at the same temperature as that at which the activity was observed. The temperature, as will be seen, varied to some extent, but we found that the variation did not have any considerable effect on the specific rotation. The ethereal salts examined were the methylic, ethylic, propylic, and normal butylic methoxy- and ethoxy-succinates, also the isopropylic and isobutylic ethoxysuccinates, but the two latter compounds were not obtained in the pure state. In some cases, to ensure greater accuracy, both active forms were prepared; in other cases, owing to insufficient material, only one of them. As determinations of the rotatory power of active compounds are not unfrequently entirely vitiated by the substances becoming partially racemised, and as the conditions which induce this change are as yet very imperfectly known, we have thought it necessary to quote the observations on activity made after each distillation of the liquids examined.

Methylic d-*Methoxysuccinate.*

1st distillation, b. p. 146° at 75 mm.; $t = 12°$, $l = 1$, $\alpha = +60·4°$. *2nd distillation*, b. p. 132° at 40 mm.; $t = 12°$, $l = 1$, $\alpha = +60·4°$, d 12°/4° = 1·1503, $[\alpha]_D = +52·50°$. *3rd distillation*, b. p. 119°

at 22 mm.; t = 12°, l = 1, α = +60·38°, d 12°/4° = 1·1498, $[\alpha]_D$ = +52·51°.

Analysis: 100 parts required 63·7 parts KOH for hydrolysis; calculated, 63·8 parts.

The compound is liquid at 0°; the racemoïd salt is a crystalline solid melting at 28°. The specific rotatory power is somewhat too low, as the salt was made from a specimen of acid which was known to contain a little racemoïd acid.

Ethylic l-*Methoxysuccinate.*

1st distillation, b. p. 134° at 25 mm.; t = 12°, l = 2, α = −105·11° *2nd distillation*, b. p. 128° at 20 mm.; t = 10°, l = 2, α = −108·68°. *3rd distillation*, b. p. 136° at 28 mm.; t = 18°, l = 1, α = −53·64°, d 18°/4° = 1·0705, $[\alpha]_D$ = −50·11°.

Results of combustion: found, C = 52·70, H = 7·95; calculated, C = 52·94, H = 7·84 per cent.

Propylic l-*Methoxysuccinate.*

1st distillation, b. p. 157—158° at 31 mm.; t = 13°, l = 1, α = −45·3°. *2nd distillation*, b. p. 147° at 20 mm.; t = 12°, l = 1, α = −47·05°, d 12°/4° = 1·0517, $[\alpha]_D$ = −44·74°. *3rd distillation*, b. p. 173—173·5° at 58 mm.; t = 15°, l = 1, α = −47·1, d 15°/4° = 1·0419, $[\alpha]_D$ = −45·21°.

Analysis: 100 parts required 48·3 parts KOH for hydrolysis; calculated, 48·4 parts.

Normal Butylic l-*Methoxysuccinate.*

1st distillation, b. p. 171—172° at 25 mm.; t = 15°, l = 1, α = −41·58°. *2nd distillation*, b. p. 174° at 30 mm.; t = 15°, l = 1, α = −41·97°, d 15°/4° = 1·0149, $[\alpha]_D$ = −41·35°. *3rd distillation*, b. p. 172° at 25 mm.; t = 15°, l = 1, α = −42·25°, d 15°/4° = 1·0149. $[\alpha]_D$ = −41·63°.

Analysis: 100 parts required 43·2 parts KOH for hydrolysis; calculated, 43·1 parts.

Methylic d-*Ethoxysuccinate.*

1st distillation, b. p. 133° at 40 mm.; t = 13°, l = 1, α = +65·08. *2nd distillation*, b. p. 115—116° at 19 mm.; t = 13°, l = 1, α = +66·08°. *3rd distillation*, b. p. 121° at 30 mm.; t = 13°, l = 1, α = +66·17°, d 13°/4° = 1·1055, $[\alpha]_D$ = +59·86°.

Analysis: Found, C = 50·36, H = 7·63; calculated, C = 50·53, H = 7·37 per cent.

A second distinct preparation of this compound from a different specimen of active acid gave the following results after the liquid had been distilled twice B. p. 115—116° at 16 mm.; $t = 19°$, $l = 2$, $\alpha = +133\ 84°$, $d\ 19°/4° = 1\ 0990$, $[\alpha]_D = +60\ 89°$.

Methylic l-*Ethoxysuccinate.*

1st distillation, b. p. 119—120° at 19 mm.; $t = 13°$, $l = 2$, $\alpha = -135·07°$, $d\ 13°\ 4° = 1·1070$, $[\alpha]_D = -61·01$. *2nd distillation*, b. p. 119—120° at 18 mm.; $t = 13°$. $l = 2$, $\alpha = -135·34°$. *3rd distillation*, b. p. 110° at 12 mm.; $t = 12°$, $l = 2$, $\alpha = -135·46°$, $d\ 12°/4° = 1·1080$, $[\alpha]_D = -61·13°$; $t = 20°$, $l = 2$, $\alpha = -133\ 98°$, $d\ 20°/4° = 1·0996$, $[\alpha]_D = -60·92°$.

Analysis: Found, C = 50·22, H = 7·41; calculated, C = 50·53, H = 7·37 per cent.

The specific rotation, it will be seen, varies little between 12° and 20°, and the number found for the two oppositely active forms is practically the same, though the specific gravities found differ a little. The specific gravities of the active and inactive compounds are apparently identical; that of the inactive salt, the preparation of which was referred to above, was found to be $d\ 15°/4° = 1·1054$; that of the dextro-salt, quoted above, $d\ 13°/4° = 1·1055$.

Ethylic d-*Ethoxysuccinate.*

1st distillation. b. p. 132—134° at 18 mm.; $t = 14°$, $l = 2$, $\alpha = +115·79°$. *2nd distillation.* b. p. 125° at 14 mm.; $t = 12°$, $l = 2$, $\alpha = +116·72°$, $d\ 12°/4° = 1·0479$, $[\alpha]_D = +55·69°$. *3rd distillation*, b. p. 124° at 13 mm.; $t = 12°$, $l = 2$, $\alpha = +116\ 52°$, $d\ 12°/4° = 1·0475$, $[\alpha]_D = +55·62°$; $t = 17°$, $l = 2$, $\alpha = +115·73°$, $d\ 17°/4° = 1·0418$, $[\alpha]_D = +55·54°$. It will be seen that the specific rotation is practically the same at 12° and at 17°. A second specimen made from another preparation of active acid, gave almost the same result. $t = 17°$, $l = 2$, $\alpha = +115·2°$, $d\ 17°/4° = 1\ 0418$, $[\alpha]_D = +55·29$.

Analysis: Found, C = 54 98, H = 8 39; calculated, C = 55·05, H = 8 26 per cent.

As the percentage composition of this salt is not far removed from that of the corresponding fumarate, it was also hydrolysed quantitatively; 100 parts required 51·8 parts KOH; calculated, 51·5 parts.

The inactive and active salts have evidently the same specific gravity; that of the inactive salt (see above) was found to be $d\ 17°/4° = 1·0403$.

Propylic d-*Ethoxysuccinate.*

1st distillation, b. p. 151° at 16 mm.; $t = 11°$, $l = 2$, $\alpha = +102{\cdot}12°$. *2nd distillation*, b. p. 147—148° at 12 mm.; $t = 12°$, $l = 2$, $\alpha = +103{\cdot}97°$, $d\,12°/4° = 1{\cdot}0169$, $[\alpha]_D = +51{\cdot}12°$. *3rd distillation*, b. p. 144° at 11 mm.; $t = 15°$, $l = 2$, $\alpha = +103{\cdot}97°$, $d\,15°/4° = 1{\cdot}0131$ $[\alpha]_D = +51{\cdot}31°$.

Analysis: Found, C = 58·47, H = 9·01; calculated, C = 58·54, H = 8 94 per cent.

Propylic l-*Ethoxysuccinate.*

1st distillation, b. p. 157—158° at 25 mm. The liquid being coloured with iodine, was shaken up with a little mercury, diluted with anhydrous ether and filtered. *2nd distillation*, b. p. 146—149° at 14—16 mm.; $t = 9°$, $l = 1$, $\alpha = -52{\cdot}08$, $d\,9°/4° = 1{\cdot}0223$, $[\alpha]_D = -50{\cdot}93°$. *3rd distillation*, b. p. 147° at 17 mm.; $t = 7°$, $l = 1$, $\alpha = -52{\cdot}36°$, $d\,7°/4° = 1{\cdot}0226$, $[\alpha]_D = -51{\cdot}20°$.

Analysis: 100 parts required 45·1 parts KOH for hydrolysis; calculated, 45·6 parts.

Normal Butylic l-*Ethoxysuccinate.*

1st distillation, b. p. 161° at 15 mm.; $t = 6°$, $l = 1$, $\alpha = -46{\cdot}68°$, $d\,6°/4° = 1{\cdot}0053$, $[\alpha]_D = -46{\cdot}43°$ *2nd distillation*, b. p. 158° at 13 m.m.; $t = 6°$, $l = 1$, $\alpha = -46{\cdot}7°$, $d\,6°/4° = 1{\cdot}0045$, $[\alpha]_D = -46{\cdot}43°$.

Analysis: 100 parts required 40·5 parts KOH for hydrolysis; calculated, 40·9 parts.

Isopropylic d-*Ethoxysuccinate.*

During the action of isopropylic iodide on the silver salt, the formation of a hydrocarbon, probably isopropylene, was detected. The distillate was highly coloured with iodine; it was therefore diluted with anhydrous ether, shaken with a little mercury, and filtered. The liquid was twice redistilled, but did not boil constantly like the other salts. Two fractions were collected, one at 153—155°, and the other at 158—172° under 25 mm. pressure. The observations made on the lower boiling fractions were as follows: $t = 15°$, $l = 1$, $\alpha = +51{\cdot}77°$, $d\,15°/4° = 1{\cdot}0217$, $[\alpha]_D = +50{\cdot}67°$. The higher boiling fraction was strongly acid, and gave the rotation +56° in the 100 mm. tube at 6°. The substance was evidently impure, and there was too little of it for us to attempt to purify it.

Isobutylic d-*Ethoxysuccinate.*

In this case also a hydrocarbon, probably isobutylene, was formed during the action of the isobutylic iodide on the silver salt. *1st distillation*, b. p. of main fraction, 176—190° at 42 mm.; $t = 15^\circ$, $l = 1$, $\alpha = +57{\cdot}65^\circ$. *2nd distillation*, b. p. 165—175° at 19 mm; $t = 15^\circ$, $l = 1$, $\alpha = +57{\cdot}37^\circ$, $d\,15^\circ/4^\circ = 1{\cdot}0832$, $[\alpha]_D = +52{\cdot}96^\circ$. *3rd distillation*, b. p. 156—162° at 14 mm.; $t = 15^\circ$, $l = 1$, $\alpha = +54{\cdot}00^\circ$, $d\,15^\circ/4^\circ = 1{\cdot}0485$, $[\alpha]_D = +51{\cdot}50$. The liquid was a viscid syrup, and in this respect differed from all the other salts which were mobile liquids. It was observed that for some hours after distillation the activity continued to increase, though the temperature of the liquid remained the same; the angles of rotation recorded were observed about 12 hours after distillation. The liquid was evidently not pure, as it had an acid reaction, and the highest boiling fraction in the last distillation deposited crystals of *d*-ethoxysuccinic acid on standing. The compound was not analysed.

Isobutylic l-*Ethoxysuccinate.*

1st distillation, b. p. about 178° at 25 mm.; the liquid was highly coloured with iodine. *2nd distillation*, b. p. 167—168° at 12 mm.; $t = 11^\circ$, $l = 2$, $\alpha = -114{\cdot}52^\circ$, $d\,11^\circ/4^\circ = 1{\cdot}0741$, $[\alpha]_D = -53{\cdot}31^\circ$. *3rd distillation*, b. p. 167—169° at 13 mm.; $t = 15^\circ$, $l = 1$, $\alpha = -56{\cdot}65^\circ$, $d\,15^\circ/4^\circ = 1{\cdot}0669$, $[\alpha]_D = -53{\cdot}10^\circ$. This ethereal salt also contained free acid, and the observations of its activity are not very trustworthy. Considering, however, the agreement between the numbers obtained for the two oppositely active compounds, we are inclined to think that the specific rotation is probably approximately correct.

The fairly concordant rotations found for the oppositely active isomerides, and for different preparations of the same isomeride, show pretty clearly that the compounds did not undergo racemisation in the course of the processes through which they passed. To obtain more conclusive evidence on this point, some of the dextrorotatory ethoxysuccinates were hydrolysed with barium hydroxide, and from the barium salt the acid was procured in the usual way by treating it with the calculated quantity of sulphuric acid. The ethereal solution of the acid crystallised in colourless prisms having the same melting point, and nearly the same specific rotation as the original acid. The following were the observations made on it: $t = 17^\circ$, $l = 2$, $c = 22{\cdot}4885$, $\alpha = +15{\cdot}37^\circ$, $[\alpha]_D = +34{\cdot}18^\circ$; $t = 17^\circ$, $l = 2$, $c = 13{\cdot}3980$, $\alpha = +9{\cdot}04^\circ$, $[\alpha]_D = +33{\cdot}74^\circ$; the specific rotations of one of the original specimens of acid for similar concentrations were +34·73° and 34·41°, and of another 34·06° and 33·85°. Some of the lævorotatory ethoxysuccinates were also hydrolysed, and the acid obtained from them converted into acid ammonium salt, which gave the following rotation : $l = 2$, $c = 4{\cdot}862$, $\alpha = -2{\cdot}79$, $[\alpha]_D = -28{\cdot}69°$. The salt, before conversion into ether, had the specific rotation, 28·88° at the same concentration. Active methoxysuccinic acid was also recovered from the ethylic *l*-methoxysuccinate; it was found to have the specific rotation $[\alpha]_D = -31{\cdot}75°$ ($c = 15{\cdot}15$), the highest number found for the original acid being −32·70. These results show that the active acids did not become racemised by their etherification and subsequent treatment. The somewhat low activity of the recovered methoxysuccinic acid is due to the fact that the acid from which the ethereal salt was made was not quite so active as the specimen whose rotation is quoted.

Discussion of Results.

The striking points in the activity of the alkyloxysuccinic acids are the constancy of their specific rotatory powers in aqueous solution for wide ranges of concentration, and the enormous increase which these exhibit in organic solvents. Thus in the case of ethoxysuccinic acid, the specific rotatory power in aqueous solution varies only a few tenths of a degree between the concentrations 20 and 2 per cent., and rises from about 35° in water to about 70° in ethylic acetate, the rotation of the latter solutions remaining also fairly constant with varying concentration. In acetone the specific rotatory power is a little less than in ethylic acetate and rises slightly with dilution, in alcohol it is still further lowered to about 60·5°, and in chloroform it undergoes not only a much greater diminution, but exhibits also much greater variation with changing concentration. The rotation for example falls from 47·7° for $c = 11{\cdot}6$ to 39·4 for $c = 1{\cdot}5$. So far as the observations go which are recorded in the preceding paper, methoxy- and propoxysuccinic acids exhibit exactly parallel phenomena. With respect to its effect on the activity of the acid, chloroform appears to stand in a different category from the other organic solvents used, and this accords with the observations of Freundler (*Compt. rend*, 1893, **117**, 556), who found that oxygenated solvents in general had little influence on the rotatory powers of the ethereal diacidyltartrates, whilst haloïd derivatives tended to reduce their value.

The question arises, which of the observations on solutions, if any, can be taken to represent the actual activity of the acids? The high values found in organic solvents cannot, we think, be so regarded for the following reason: the rotations of even concentrated aqueous solutions are nearly the same as those of the semi-dissociated and not very far above those of the wholly dissociated acids, as determined by observations on dilute solutions of the acid and normal salts of the alkalis respectively, and if the acids exist in organic solvents in the condition of unassociated molecules, then to account for the comparatively low rotation in water solutions it would be necessary to attribute to these solutions a much greater extent of electrolytic dissociation than can be readily supposed to have occurred. The following determinations of the molecular weight of the acid in aqueous solution made by the freezing point method show that no such abnormal amount of dissociation does take place. I. P. = 8·6152, $\Delta = 1·025°$, hence M = 158·9. II. P = 1·6402, $\Delta = 0·221°$, hence M = 140·3. Calculated, M = 162. The specific rotations of the solutions were 34·51° and 34·72° respectively. It follows that the high activity of the acids in organic solvents must be due either to the existence in the solutions of molecular compounds with the solvent, which was the view held by Biot with regard to phenomena of the kind under discussion, or to the presence of associated molecules which have a higher rotatory power than the simple molecules. The latter explanation in view of recent research seems the more probable, and in the present case the fact that such different solvents as acetone and ethylic acetate have approximately the same influence on the activity points to the same conclusion, though the comparatively slight change of activity produced by change of concentration might be held to militate against this view. It is, perhaps, worthy of notice that the rotations of methoxy- and ethoxy-succinic acids in acetone are just about double their respective rotations in water; the same remark applies to acetylmalic acid, the specific rotatory power of which according to Guye (*Compt. rend*, 1893, **116**, 1135) is in water —10·4° to —10·7° and in acetone —21° to —25·8°, and the same relation holds approximately for malic acid the specific rotatory power of which varies in water from —2·30° for $c = 8·4$ to —3·06° for infinite dilution, and in acetone according to Guye has the value —5·7°.

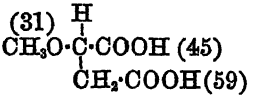
The alkyloxysuccinic acids, judging from their relation to malic acid, should undergo a considerable amount of electrolytic dissociation in dilute aqueous solution, and the second freezing point determination quoted above indicates that this is so; as the specific rotation of the acids, however, is independent of concentration, it follows that their activity must be about the same as that of the products of their dissociation. That this is really the case is shown by a comparison of the specific rotatory powers of the acids in about 8 per cent. aqueous solution with those of the respective ions,

$$CO_2HCH_2\cdot CHOC_nH_{2n+1}\cdot CO\bar{O},$$

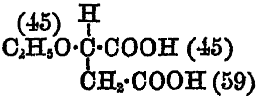
found from observations on dilute solutions of the acid salts of the alkalis. It will be noticed that the difference between the rotation of the acid and of the ion amounts to only about 2°. In the case of the methoxy-acid the low number found for the ion is probably due to the fact that the salt from which it was deduced was not examined in sufficiently dilute solution.

	Methoxy.	Ethoxy.	Propoxy.
Acid	32·5	34·5	36·2
Ion	29·5	36·0	39·5

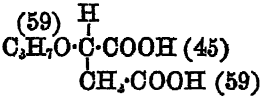
From these considerations we think that the specific rotatory powers of the acids in aqueous solution may be taken as an approximate measure of the actual activity of the substances. An inspection of the weights of the radicles attached to the asymmetric carbon atoms,



$$\begin{array}{l}(31)\ \mathrm{H}\\ \mathrm{CH_3O\cdot C\cdot COOH\ (45)}\\ \qquad\quad \mathrm{CH_2\cdot COOH(59)}\end{array}$$



$$\begin{array}{l}(45)\ \mathrm{H}\\ \mathrm{C_2H_5O\cdot C\cdot COOH\ (45)}\\ \qquad\quad \mathrm{CH_2\cdot COOH\ (59)}\end{array}$$



$$\begin{array}{l}(59)\ \mathrm{H}\\ \mathrm{C_3H_7O\cdot C\cdot COOH\ (45)}\\ \qquad\quad \mathrm{CH_2\cdot COOH\ (59)}\end{array}\ .$$

shows that the simpler form of Guye's hypothesis according to which the masses of the radicles are the chief factors influencing activity, while other factors, such as length of lever arm and possible distortion of the regular tetrahedron, are regarded as having only a subordinate influence, is inadequate to explain the phenomena exhibited by these acids. There being two equal masses in both the ethoxy- and propoxysuccinic acids, these substances should be inactive. All three acids possess in reality a high activity, which increases uniformly with increase of the oxyalkyl group. It appears, therefore, that between these groups and the CO_2H or $CH_2\cdot CO_2H$ group, there exists such an essential difference, that, though they are of equal mass, molecules containing them may yet possess a high degree of dissymmetry, in the production of which, therefore, the mass of the radicles plays only a subordinate part. The case of ethoxy- and propoxy-succinic acids is exactly analogous to that of methylic and ethylic diacetylglycerates described by Frankland and Macgregor (*Trans.*, 1893, 63, 1419); in both instances two successive members of a homologous series contain each two groups of equal mass, and yet there is no indication of any near approach to a change of sign in the series. It should be stated that Guye, even in his first memoir saw reason to conclude that in compounds containing radicles of equal weight, it would be necessary to take into account other factors besides mass, and that he has not ceased to emphasise the important part which such factors may play. It is, however, difficult to conceive any valid reason why such factors should affect the rotatory power of molecules to a greater extent when they contain radicles of equal mass than when the masses of all the radicles are different, and it is, therefore, surprising that the simpler form of the hypothesis should apparently suffice to predict successfully the position of maximum activity in a series like the glycerates, and yet give such erroneous deductions regarding positions of minimum activity in similar series such as the diacetylglycerates.

Objections may perhaps be taken to our use of the results derived from observations on aqueous solutions of the free acids, notwithstanding the considerations we have advanced in support of their availability as measures of the actual rotatory powers of the compounds. It may be pointed out, supposing such objections to be valid, that observations on dilute aqueous solutions of the normal salts of the alkalis, which in the opinion of van't Hoff is probably the only method of obtaining comparable results for acids, lead to conclusions similar to those deduced above. Hitherto, so far as we know, no observations of this kind have been made on closely allied acids, and we append, therefore, a note of the ionic specific rotatory powers of the three acids calculated from observations made on solutions of the normal ammonium and potassium salts,

Methoxy.	Ethoxy.	Propoxy.
14·86°	22·41°	27 09°

from which it will be seen that the rotation rises uniformly as in the observations made with the acids.

Turning now to the ethereal salts, we tabulate below the specific rotatory powers of the compounds examined, their molecular rotations, and the corresponding products of asymmetry calculated from Guye's simplified formula,

$$P = \frac{(a-b)(a-c)(a-d)(b-c)(b-d)(c-d)}{(a+b+c+d)^6}.$$

We have omitted the sign of rotation, and taken the mean of duplicate experiments on the same form, or on oppositely active forms, except when we had reason to believe that certain results were more reliable than others. The specific gravities being taken at varying temperatures, are omitted; the values decrease, as was to be expected, with ascending series, and are lower in the ethoxysuccinates than in the corresponding methoxysuccinates.

Methoxysuccinates.

	$[\alpha]_D$.	$[\alpha]_D \frac{M}{100}$.	$P \times 10^6$.
Methylic........	52·51	92·42	106
Ethylic.........	50·11	102·22	122
Propylic........	45·21	104·89	125
Butylic.........	41·63	108·24	121

Ethoxysuccinates.

	$[\alpha]_D$.	$[\alpha]_D \frac{M}{100}$.	$P \times 10^6$.
Methylic........	60·98	115·86	32
Ethylic.........	55·48	120·95	59
Propylic........	51·25	126·08	76
Butylic.........	46·43	127·22	85
Isopropylic......	50·67	124·65	—
Isobutylic......	53·00	145·22	—

The sign of rotation of the compounds is the same as that of the acids from which they were derived. Leaving out of account for the present the isopropylic and isobutylic salts, which are not comparable with the others, the specific rotations decrease and the molecular rotations increase in each series with increasing molecular weight. The specific and molecular rotations of the ethoxysuccinates are higher than those of the corresponding methoxysuccinates, as was to be expected from the relations of the acids. On plotting out the specific rotations, we find that the values for each series, excepting that of methylic methoxysuccinate, lie on nearly straight lines which are approximately parallel. The specific rotation of the salt mentioned is about 2° lower than it should be; it was made, as already stated, from a specimen of acid somewhat less active than that from which the other three members ot the series were procured.

The addition of CH_2 to the two carboxyl groups lowers the specific rotatory power by more or less the same amount as the addition of CH_2 to the oxyalkyl group raises it. It will be noticed further that the molecular rotations of the methoxysuccinates show a tendency to attain a maximum, making allowance for the low rotation of the first member, the difference between that of the first and second is about 6°, and between that of the propylic and butylic members 3·3°. This tendency is distinctly marked in the ethoxysuccinates where the maximum is probably reached by the butylic compound.

It remains to inquire how far the simpler form of Guye's hypothesis will account for these facts. The increase of activity on converting the acids into ethereal salts is evidently in conformity with the hypothesis, as the masses of the two radicles which are already the highest are thereby increased, but we cannot attach much importance to this point, as it is doubtful whether observations on liquid ethereal salts and acids in solution are strictly comparable. The increase of molecular rotation with increase of molecular weight is also in accordance with the hypothesis, for the calculated products of asymmetry increase in both series. It should be noted, however, that the specific rotations vary in the opposite sense. We may remark here that in another series, that of the amylic salts of the fatty acids (*Compt. rend.*, 1894, **119**, 906), the specific rotations of which attain a maximum at a point near to that indicated by the product of asymmetry, give very different results if the molecular rotations, which are strictly the proper measures of varying activity, are compared. The increase of rotation on passing from the methoxy- to the ethoxy-succinates is not predicted by the product of asymmetry, for the value of P in the ethoxy series is much lower than in the methoxy series within the range of the members examined. It will be seen that the value of P in the methoxy series attains a maximum at the propylic compound; the experimental maximum must be considerably higher in the series; the calculated and experimental maxima in the ethoxy series are not far removed from each other, as the former falls on the hexylic and the latter on the butylic or amylic salt. As already stated, we do not attach much importance to the results obtained with the isopropylic and isobutylic compounds, as they were not pure; it may be pointed out, however, that the isopropyl radicle seems to act more strongly and the isobutyl less strongly in lowering the specific rotation than the corresponding normal radicles; in the case of the glycerates, diacetyl glycerates, and diacidyl tartrates (*Bull. Soc. Chim.*, 1894, **11**, 370) the differences are of a similar kind, but in the opposite sense; the isopropyl radicle acting less strongly and the isobutyl more strongly in raising the rotation. This review of the results of our experiments leads us on the whole to conclude that, in order to explain the phenomena exhibited by the alkyloxysuccinic acids and their ethereal salts, other factors besides mass must be taken into account. An extensive investigation by Walden on active derivatives of succinic acid, just published (*Zeit. physikal. Chem.*, 1895, **17**, 245), leads to the same conclusion.

The great increase of activity produced by the replacement of the OH-group in malic acid by an oxyalkyl group, and the discrepancies between the experimental results and the requirements of Guye's hypothesis in its simpler form, have led us to attempt to find the order of the values or coefficients of asymmetry, as they might be called, of the radicles H, OC_nH_{2n+1}, COOH, and $CH_2{\cdot}COOH$. Starting with the provisional assumption that in malic acid the values of the coefficients of H, OH, COOH, and $CH_2 \cdot COOH$ are in the same order as their masses, and that in methoxysuccinic acid, H and $CH_2 \cdot COOH$ retain their relative position, the relative magnitude of OCH_3 and COOH remains still in doubt. The preparation of methoxysuccinic acid from malic acid would of course decide the question of the relation of these groups, for if the former were greater than the latter a change of sign would then result; as already stated, our efforts in this direction have not met with success. We therefore tried to connect the alkyloxysuccinic acids with the active halogen succinic acids. The experiment was made by way of trial on inactive methoxysuccinic acid; on heating it at 100° with concentrated hydrochloric acid, the substance remained unchanged; on heating it with fuming hydrobromic acid, bromosuccinic acid was formed, but with it some fumaric acid, and this only after heating the mixture at 130—140°, so that the method could not be applied evidently with any chance of success to the active acid. Among the numerous active derivatives of succinic acid recently described by Walden (*loc. cit.*) is a lævorotatory ethylic ethoxysuccinate, presumably prepared from ethylic malate. No description of its preparation or other details have yet been published, but as its specific rotatory power is only 1·44°, while the actual rotation of the compound, according to our experiments, is about 55°, our experience leads us to conclude that Walden's substance is probably inactive ethylic ethoxysuccinate contaminated with small quantities of ethylic malate.

In default of direct evidence, the following considerations incline us to conclude that the coefficient of $\cdot OCH_3$ is probably greater than that of ·COOH, in spite of the smaller mass. As the ethereal malates increase in activity with ascending series, derivatives formed from them by replacement of the ·OH-group by radicles of higher value, without change of sign occurring, should also increase in activity with ascending series, and should probably diminish in activity with further loading of the ·OH-group, whilst, on the other hand, derivatives similarly formed, but with reversal of sign, should exhibit the reverse phenomena. The acidyl ethers of malic acid belong apparently to the first class; increase at the carboxyl group produces very slight change, increase of the acidyl group produces a slight fall of activity. The ethereal halogen-succinates, on the other hand, evidently belong to the second class; a reversal of sign occurs in their production from the malates, and, as was to be expected, their activity diminishes with ascending series, whilst the members of the bromine series have a higher activity than corresponding members of the chlorine series. The activity of the ethereal alkyloxysuccinates also decreases with ascending series, and increases with increase of the oxyalkyl group; it is therefore probable that in their production from the malates a change of sign will be found to occur, and that the value of OCH_3 is greater than that of COOH or even of $COOCH_3$. This deduction is based upon specific rotations, but the molecular rotations also indicate that in respect of the change of activity which occurs with ascending series, the ethereal alkyloxysuccinates show more resemblance to the halogen-succinates than to the malates or acetylmalates.

Secondly, the substitution of CH_3 for H in OH commonly produces a much greater change of general physical properties than the substitution of alkyl groups for one another under similar conditions; now, considering the ionic rotations of the normal salts of *d*-malic and *d*-alkyloxysuccinic acids,

	d-malic.	Methoxy.	Ethoxy.	Propoxy.
Normal salt....	+14°	+14·8°	+22·4°	+27·1°

which are the most reliable constants for comparison, it is evident that if *d*-methoxysuccinic acid is derived from *d*-malic acid, a much larger change of activity is produced by replacing CH_3 by C_2H_5 or C_2H_5 by C_3H_7 than by replacing H by CH_3, which is the reverse of what might be expected. If, however, *d*-methoxysuccinic acid is derived from *l*-malic acid, then, in passing from the ion of the latter to that of the former a change of about 29° occurs, which conforms better with known experimental facts.

The evidence advanced supports the conclusion that the OCH_3, OC_2H_5, and OC_3H_7 groups possess higher coefficients of asymmetry than the group COOH, and lower coefficients than $CH_2{\cdot}COOH$. Similar considerations would, we think, explain the various anomalies exhibited by the numerous derivatives of malic acid prepared by Walden; thus the values of the halogens, when directly united to the asymmetric carbon atom, must evidently be taken as greater, irrespective of all considerations of mass, than those of acidoxyl and carboxyl groups. It must, however, be confessed that the slight effects on activity produced in the ethereal acetylmalates by enormous changes in the masses of the radicles is extremely puzzling, and suggests the conclusion that before Guye's law of the product of asymmetry can be applied even qualitatively with success, it will be necessary to make some approach to a knowledge of the relative values of the radicles by some such method as that attempted above, as was originally proposed by Crum-Brown.

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University of St. Andrews.

XCVIII.—*Rate of Escape of certain Gases from Solutions of varying Concentration. Addendum.*[*]

By Edgar Philip Perman.

The President suggested that an arithmetical method of differentiation might be used with advantage instead of the graphical method described in my paper (*Trans.*, 1895, **88**, 868), and he very kindly found a formula which accurately reproduces the values of Q (amount of ammonia in solution in grams) given on page 871; it is $\log Q = 0{\cdot}646 - 0{\cdot}00352\, t$ (t = time, in minutes, from the beginning of aspiration).

The comparison stands thus:—

Time in minutes. t.	NH_3 in solution. Observed.	NH_3 in solution. Calculated.
0	4·43	4·43
15	3·90	3·92
30	3·45	3·47
45	3·07	3·08
60	2·72	2·72
80	2·33	2·32
90	2·15	2 14
105	1·90	1·89

By differentiation the rates of escape are obtained. The following table shows the values obtained by both methods:—

NH_3 in solution. Grams.	By the arithmetical method. Milligrams per min.	By the graphical method. Milligrams per min.
4·2	34·0	35·1
3·8	30·8	31·6
3·4	27·5	27·5
3·0	24·3	23·7
2·6	21·1	20·5

The agreement is not so close as could be wished, but sufficiently close to show that the graphical method is fairly accurate. The author has found that the results given by the two methods usually agree better, and never worse, than those in the preceding table.

The sentences in the paragraph following Fig. 2 on p. 871 (line 4 from bottom *et seq.*) were transposed by mistake; it should read:—

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[*] The subject-matter of this addendum was intended to form part of the original paper (pp. 868—880), but was omitted owing to a mistake for which Dr. Perman is in no way responsible.—Eds.

"As before explained, the values of the tangents are proportional to the gas-pressures, and therefore Henry's law appears from these results to hold good for ammonia between concentrations of 48 grams and 88 grams per litre. In order to test the validity of the law by this method, through the greatest possible range, concentrated ammonia solution was treated in a similar manner. The Qt curve was quite smooth (Curve 1, Fig. 3); it was re-drawn in two portions to ensure greater accuracy in drawing tangents, the values of which were then plotted on one curve (Curve II, Fig. 3). It is not straight, but deviates more and more from a straight line as concentration increases. The values of Q cannot be expressed by any simple equation. The curve is, however, practically straight between any two points for which the concentration varies not more than 2 grams in 50 c.c."

XCIX.—*Note on the Reduction of Potassium Platinochloride.*

By EDWARD SONSTADT.

THE usual laboratory method of reducing the platinochlorides of potassium and other alkali metals by hydrogen is effective, although inconvenient and requiring some preparation; moreover it is not readily applicable to larger quantities than can be placed in a porcelain boat within a glass tube. The method I have now to offer is thoroughly effective at a temperature below a red heat, and can be conveniently used on any quantity of the salt.

When potassium platinochloride, for instance, is rubbed up with about twice its weight of mercury (in the same manner that chalk and mercury are rubbed together to form the well-known compound "mercury with chalk") and the mixture is gently heated, calomel sublimes, together with the excess of mercury, leaving a very porous mass of platinum and potassium chloride, which can be quickly washed. The reduction is complete, no trace of undecomposed platinum salt remaining, and if the mercury used is pure, no foreign element is introduced. If the platinum salt and mercury are taken in approximately equal weights, the sublimate consists chiefly of corrosive sublimate, but the reduction is also complete in this case. The following equations represent the reactions.

(1.) $2KCl,PtCl_4 + 4Hg = 2KCl + Pt + 4HgCl.$

(2.) $2KCl,PtCl_4 + 2Hg = 2KCl + Pt + 2HgCl_2.$

With small, accurately weighed quantities of the platinochloride, it is more convenient to place an excess of mercury (which need not be a great excess) in a small porcelain crucible, and then to add the platinum salt; heat is applied very gently for some time, and 'terwards raised sufficiently to volatilise the sublimate adhering to the sides of the crucible, and to drive off the excess of mercury. It hardly necessary to add that the heating should be conducted ithin a chamber adapted for carrying off the fumes, or, if con- erable quantities are under treatment, that provision should be de for collecting the sublimate.

Mercury, when agitated with solution of a platinum salt, precipitates the platinum, as it does many other metals from their solutions. The reaction is very delicate, so much so, that a solution of 1 part of potassium platinochloride in 3,000,000 parts of water may be distinguished from pure water by the test, provided that the mercury is so pure as to leave no stain on a clean porcelain crucible when volatilised.

C.—*Orthobenzoicsulphinide.*

By William J. Pope.

Orthobenzoicsulphinide (commercial saccharin) is put on the market as a white micro-crystalline powder containing a considerable proportion of parasulphaminebenzoic acid. Having occasion to attempt the purification of some of the commercial article some months ago, I dissolved it in acetone, in which it is fairly soluble, and after filtration allowed the solution to evaporate spontaneously; massive, colourless rhombohedra were deposited, and when examined were found to consist of pure saccharin. A very pure and well crystallised sample of saccharin may be thus obtained from the impure commercial substance by one crystallisation from acetone; it was found to be identical with the purified material prepared by Ling's process (English Pat. of 1893, 21417) of boiling the commercial article with sodium acetate. Samples prepared by Mr. Ling, and also by myself, by this process, when crystallised from acetone, yielded crystals which were indistinguishable in properties from those obtained by once crystallising the commercial substance from acetone.

Orthobenzoicsulphinide is deposited from its cold acetone solution in colourless, transparent, monosymmetric crystals which have a vitreous lustre, and may readily be obtained 2 cm. or more in length.*

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* It does not seem to be generally known that acetone often forms a very good solvent for refractory organic substances which are required in large crystals; thus ammonium picrate, which can only be obtained in small crystals from most solvents, separates from acetone in massive transparent crystals, two or more cm. in length, which are now being examined, as their optical properties are of considerable interest.

The crystals usually affect a rhombohedral habit, being bounded by the forms $a\{100\}$ and $q\{011\}$; the pinacoïd $a\{100\}$ is usually the predominant form, but the dome $q\{011\}$ is often as largely developed. Traces of the dome $r\{\bar{1}01\}$ are generally observable, and sometimes the faces of this form are fairly large; the pinacoïd $c\{001\}$ is less frequently observed, whilst the prism form $p\{210\}$ is very rarely observed, and when present is ill-defined and gives very poor results on measurement; the forms $r\{\bar{1}01\}$ and $c\{001\}$ are generally small, and, as would be expected, usually give better measurements than the more dominant forms $a\{100\}$ and $q\{011\}$.

Crystals showing all the above forms are sometimes obtained, and then have the appearance shown in Fig. 1; butterfly-like twin-crystals (Fig. 2), in which the face of composition is $r\{\bar{1}01\}$, are sometimes deposited from the solution and triplets due to repeated twinning on faces of the same form are by no means rare.

Crystalline System. Monosymmetric.

$$a : b : c = 2 \cdot 7867 : 1 : 1 \cdot 7187.$$

$$\beta = 76° \; 8' \; 30''.$$

Forms observed :—

a	$\{100\}$
c	$\{001\}$
q	$\{011\}$
r	$\{\bar{1}01\}$
p	$\{210\}$

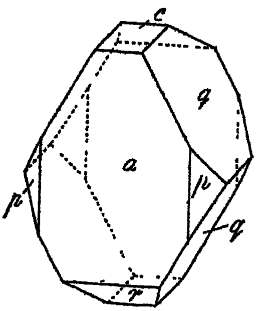

FIG. 1.

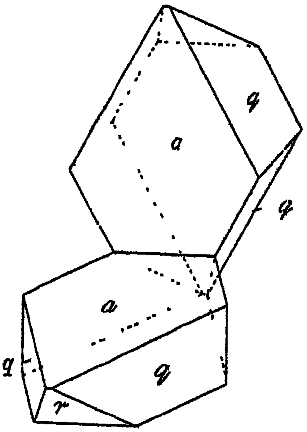

FIG. 2.

The following angular measurements were obtained :—

Angle.	No of observations.	Limits	Mean	Calculated.
$ac = 100 \cdot 001$	46	75° 46′— 76° 39′	76° 8′	76° 8′ 30″
$ar = \bar{1}00 : \bar{1}01$	54	68 5 — 69 31	68 46	—
$cr = 001 \cdot \bar{1}01$	51	34 45 — 35 37	35 5 30″	—
$ac = 100 : 00\bar{1}$	16	103 24 —104 9	103 49	103 51 30
$aq = 100 \cdot 011$	39	82 43 — 83 15	82 57	82 56
$aq = \bar{1}00 : 011$	37	96 42 — 97 31	97 3	97 4
$cq = 001 : 011$	59	58 36 — 59 48	59 4	—
$qq = 011 : 01\bar{1}$	32	61 20 — 62 29	61 52	61 52
$ap = 100 : 210$	6	52 50 — 54 1	53 24	53 32
$pp = 210 : \bar{2}10$	8	72 26 — 73 35	72 50	72 57
$pq = 210 : 011$	8	40 2 — 40 58	40 25	40 16
$qr = 011 : \bar{1}01$	15	64 39 — 65 42	65 7	65 8
$qr = 011 : 10\bar{1}$	24	114 12 —115 37	114 49	114 52

The following measurements were obtained from twin crystals:—

$aa = 100 \cdot 100$	6	42° 3′— 43° 31′	42° 40′	42° 28′
$qq = 011 \cdot 011$	8	49 12 — 50 26	49 48	49 44

On breaking or crushing the crystals, they give out a very vivid, bluish-white light, which, however, is only of momentary duration; this flashing or phosphorescence of the crystals is very brilliant, and is quite noticeable even in a well-illuminated room; it was, in fact, first observed whilst the crystals were being manipulated in the full glare of an incandescent gas lamp. The phosphorescence may be well shown on a small scale by pulverising a crystal between two microscope slides, and on a larger scale by vigorously shaking a bottle containing a few crystals in a darkened room; on grinding a quantity of the material in a glass mortar in the dark an almost continuous, though rather fainter, light is emitted. On closely watching large transparent crystals while crushing them, the illumination appears to consist of a glow which pervades the whole crystal just as it breaks, and then immediately disappears; the emission of light consequently occupies so short a time as to appear instantaneous. The phosphorescence is not always apparent, for a crystal may sometimes be crushed in the dark without becoming appreciably luminous; these cases, however, are rare; on crushing 23 crystals which had been found to be quite normal in optical and geometrical properties in the dark, only one refused to flash, although no other point of difference between it and the other crystals could be established.

The method by which the crystals are broken seems without influence on the flashing; phosphorescence occurs when the crystals are hacked with a knife, rubbed together, crushed between the fingers or between pieces of glass, and also when they are caused to crack by rapid heating, either in the air or in the acetone mother liquor from which they crystallise. There seems to be no particular plane in the crystal parallel to which breaking occurs without phosphorescence; no matter how carefully a crystal is cleaved along the very perfect cleavage on $a\{100\}$, so that parting shall only occur parallel to the cleavage, vivid phosphorescence always occurs, and on carefully cutting the crystals in the two directions perpendicular to the cleavage, so that very little parting occurs along this plane, a brilliant flash almost invariably results.

An exhaustive examination of the properties of the crystals was made in order to allow of some cause being assigned to this peculiar phenomenon; it was at first thought that the crystals might be hemimorphic or hemihedral, and that the phosphorescence might be in some way related to the polar properties inseparable from hemimorphism. Some support seemed to be given to this view by the fact that the crystals are usually very unsymmetrically developed, the forms $r\ \{\bar{1}01\}$ and $c\ \{001\}$ being frequently represented by only one face each, and a hollow often taking the place of one of the faces of the basal plane; but these anomalies can only be accidental, for such a distribution of planes does not indicate any of the kinds of symmetry possible in the monosymmetric system.

The completely holohedral nature of the crystals is shown pretty conclusively by the following methods. No evidence of pyroelectricity is obtained on heating and testing by Kundt's method; further, on cleaving a crystal parallel to $a\{100\}$ and dusting with the electrified mixture of red lead and sulphur, no indication is obtained that the two surfaces acquire a difference of electrical potential such as might be expected if this form were perpendicular to a pyroelectrical axis; no pyroelectricity is observed on heating the two cleaved surfaces. These facts seem to indicate that the phosphorescence is in no way connected with pyroelectrical polarity, for the crystals phosphoresce brilliantly when parted along the plane a (100) although no evidence of pyroelectricity is obtained from the two parted surfaces.

The strongest confirmation of the holohedral symmetry is afforded by the etch-figures obtained by corroding the various forms with solvents. For this purpose, a well developed crystal is immersed in cold acetone for a few seconds, then removed and dried between filter paper; the form $a\{100\}$, when examined under a high power, is then seen to be covered with small triangular cavities which are elongated in the direction of the c-axis; two of the edges of these figures are curved and similar, as shown in the rough sketch appended (Fig. 3), whilst the third is straight. The cavities are bounded at the bottom by three straight edges, two of which are equal in length and equally inclined to the third; the sides of the cavities are drusy and striated. The etch-figures on parallel faces are similar, but point in opposite directions; they are all symmetrical to the plane (010) The four faces of the form $q\{011\}$ when etched, become covered with small scalene triangular figures, one side of which is parallel to the axis a; the triangles are arranged as shown in the figure and those on the four faces are symmetrical to the plane (010). No characteristic figures could be obtained on the forms $p\{210\}$ and $r\{\bar{1}01\}$, but on the pinacoid $c\{001\}$, bow-shaped figures, resembling the letter D elongated vertically, are formed on etching; these are also symmetrical to the plane (010). The holohedral nature of the symmetry is thus conclusively shown by the etch-figures formed on the crystals by acetone, and very similar figures are obtained on corrosion with water.

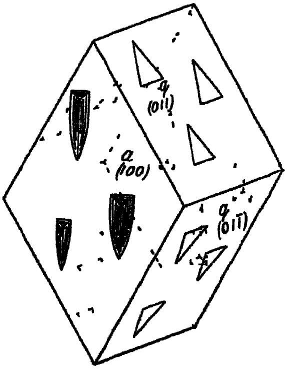

FIG. 3.

An examination of crushed crystals failed to reveal any alteration in crystallographic properties such as would be expected to result from a change in crystalline form, which is, *à priori*, a very probable cause of the peculiar phenomenon exhibited by these crystals.

It has long been known that when mica is cleaved or crystals of cane sugar are crushed, phosphorescence occurs, although the illumination obtained is excessively faint. In the case of sugar, the light can only be seen on crushing the crystals in a well-darkened room after the observer's eyes have become super-sensitised by absence of light for 10 or 15 minutes; the phosphorescence then observed appears of the same colour and character as with the aromatic compound. No case of this kind of phosphorescence has been recorded in which the phenomena at all approach the present in point of brilliancy, and further investigation of orthobenzoicsulphinide would very possibly yield an explanation of this kind of phosphorescence

Attempts to obtain phosphorescence by the rapid crystallisation of supersaturated solutions, as has been recently done by Bandrowski (*Zeit. phys. Chem.*, 1895, **17**, 234), yielded only negative results, possibly because the solutions do not lend themselves readily to rapid crystallisation. There are, however, no grounds for attributing the phosphorescence of crushed crystals and that of crystallising solutions to the same cause, and the two classes of phenomena are apparently quite distinct.

The plane of symmetry is the optic axial plane, and one optic axis emerges through $a\{100\}$ in the angle β at 43° in air to the normal; an optic axis emerges almost normally through $r\{\bar{1}01\}$, and one through $c\{001\}$ at about $47\frac{1}{2}°$ to the normal in air for sodium light; the obtuse bisectrix emerges through $a\{100\}$, and the optic axial angle is 90—100° in air. The extinctions in the faces perpendicular to the plane of symmetry are parallel to the traces of the latter; the extinction in $q\{011\}$ makes 48° with the edge aq, and 30° with the edge qc for yellow light. The double refraction is negative and very strong, and the dispersion is feeble. There is a very perfect cleavage parallel to $a\{100\}$, and the cleavage surfaces are faintly striated parallel to the b-axis; traces of the characteristic etch-figures can also be seen on them.

On heating orthobenzoicsulphinide in a current of air, a sublimate, consisting of long, colourless, glistening needles, is obtained; these are crystallographically identical with the crystals described above, and show the forms $a\{100\}$ and $q\{011\}$.

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CI.—*Derivatives of β-Resorcylic acid.*

By A. G. Perkin, F.R.S.E.

Introductory.

The following investigation was originally instituted with the object of gaining some insight into the constitution of certain natural colouring matters, but, owing to pressure of other work, it has been laid aside from time to time, and it has thus unfortunately happened that some of the results have been anticipated by others. It seemed desirable, therefore, to lay before the Society an account of such new products as have been obtained, more especially as the results attained did not serve the purpose for which they were originally intended.

The action of methylic iodide on the alkaline sodium salt of β-resorcylic acid does not yield the dimethyl ether of the methylic salt of this acid, $C_6H_3(OMe)_2·COOMe$, the principal product being a substance having the same composition, namely, $C_{10}H_{12}O_4$, and insoluble in alkalis; it, however, contained only two methoxy-groups, one of which is present in the COOMe group. It appeared, therefore, that the constitution was represented by the formula,

$$C_6H_2Me(OMe)(OH)·COOMe.$$

Crystallised from alcohol, it formed prismatic needles, melting at 76—77°. By hydrolysis, the acid itself, $C_6H_2Me(OMe)(OH)·COOH$, was obtained; this crystallises in slender needles, melting at 210°, soluble in alkalis, and containing one methoxy-group.

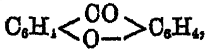
That portion of the product of the methylation of β-resorcylic acid which was soluble in alkalis consisted chiefly of two substances, one of which melted at 210°, and proved to be the acid just mentioned. The other, which was more readily soluble, was found to be the monomethyl ether of β-resorcylic acid, [COOH : OH : OCH_3 = 1 : 2 : 4], previously obtained by Tiemann and Parrisius (*Ber.*, 1885, **13**, 2375). The presence of this substance indicates that the hydroxyl group in β-resorcylic acid which resists methylation is in the ortho-position relatively to the carboxyl group.

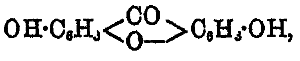
The behaviour of the alkaline sodium salt of β-resorcylic acid towards ethylic iodide is also peculiar, the principal product formed contains but two ethoxy-groups, and has apparently the constitution of a monethylic ether of the ethylic salt of β-resorcylic acid, $C_6H_3(OEt)(OH)\cdot COOEt$. In this case, contrary to what takes place when methylic iodide is used, there is no displacement of a hydrogen of the nucleus by an ethyl group.

By saponification it is converted into the acid,

$$C_6H_3(OEt)(OH)\cdot COOH,$$

melting at 153—154°. That portion of the product of the ethylation soluble in alkali consisted chiefly of the free acid, m. p. 153—154°, there being also present a trace of a substance of lower melting point.

It being important to determine the position of the ethyl group in the above ethyl ether of the acid, its behaviour towards acetic anhydride was studied. It has been shown by W. H. Perkin (Trans., 1883, 35), that when salicylic acid is distilled with acetic anhydride, diphenylene ketone oxide,  $C_6H_4{<}\substack{CO\\O}{>}C_6H_4$, is produced. β-Resorcylic acid under similar conditions yields iso-euxanthone,



$$OH\cdot C_6H_3{<}\substack{CO\\O}{>}C_6H_3\cdot OH,$$

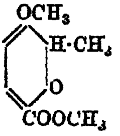
and it appeared evident that if the monethyl ether in a similar way yielded iso-euxanthone diethyl ether, it must have the constitution, OEt : OH : COOH = 1 : 3 : 4. On making the experiment such was found to be the case. Iso-euxanthone diethyl ether forms nearly colourless needles, melting at 185°. It is therefore evident that the hydroxyl group in β-resorcylic acid which resists ethylation is the one in the ortho-position relatively to the carboxylic group. It is interesting to notice that these peculiar results are due in this instance to the influence of the carboxyl group, for resorcylaldehyde when methylated behaves normally, giving the dimethyl ether,

$C_6H_3(OMe)_2{\cdot}COH$, and diethyl ether (Tiemann and Parrisius, *loc. cit*). These, when oxidised, yield the corresponding derivatives of the acid, $C_6H_3(OMe)_2{\cdot}COOH$, &c., which, as shown above, are not formed by its direct methylation or ethylation. According also to the results of Habermann (*Ber.*, 1877, **10**, 868) resorcinol dimethyl ether, $C_6H_4(OMe)_2$, is readily formed.

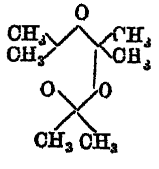
I have also studied the action of methylic iodide on resacetophenone, but unfortunately these results have been anticipated by Gregor (*Monatsh.*, 1894, **15**, 437), and Wechsler (*ibid.*, **15**, 239). With methylic iodide, resacetophenone yields a substance having the constitution, $C_6H_2Me(OMe)(OH){\cdot}CO{\cdot}CH_3$, insoluble in alkalis, the results resembling, therefore, those obtained with β-resorcylic acid. Curiously, however, the action of ethylic iodide gives a normal result, resacetophenone diethyl ether being formed. The distinctive behaviour of these substances on methylation and ethylation is exhibited more clearly by the following table.

β-Resorcylic acid, $C_6H_3(OH)_2{\cdot}COOH$, yields
$C_6H_2Me(OMe)(OH){\cdot}COOMe$ and $C_6H_3(OEt)(OH){\cdot}COOEt$.
Resacetophenone, $C_6H_3(OH)_2\,CO{\cdot}CH_3$, yields
$C_6H_2Me(OMe)(OH){\cdot}CO\,CH_3$ and $C_6H_3(OEt)_2{\cdot}CO\,CH_3$.
Resorcylic aldehyde, $C_6H_3(OH)_2{\cdot}COH$, yields
$C_6H_3(OMe)_2{\cdot}COH$ and $C_6H_3(OEt)_2{\cdot}COH$.
Resorcinol, $C_6H_4(OH)_2$, yields $C_6H_4(OMe)_2$.

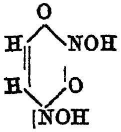
It appears probable that the insolubility in cold alkali of the methyl ethers of resorcylic acid and resacetophenone, which apparently contain a free hydroxyl group, is due to the oxygen of the latter having assumed the ketonic form. The constitution of these substances would therefore be thus represented.



Somewhat analogous to the above is the behaviour of phloroglucinol, which yields a triacetyl derivative, a trioxime, a hexamethyl derivative (Margulies, *Monatsh.*, 1888, **9**, 1046),



and a hexethyl derivative (Herzig, Zeisel, *ibid.*, **9**, 896). Though resorcinol does not react with hydroxylamine (Baeyer, *Ber.*, 1886, 19, 163), yet on treatment with nitrous acid it is converted into dinitrosoresorcinol, which can be regarded as diquinoyldioxime,



in that by treatment with hydroxylamine it now reacts with it, yielding diquinoyltetroxime (Kostanecki, *Ber.*, 1889. 22, 1345).

A preliminary investigation of the action of methylic iodide on the sodium salt of gallacetophenone has been made; the principal product, which forms colourless needles melting at 77—78°, has the constitution of a gallacetophenone dimethyl ether.

The study of the above substance is being continued, and at the same time the action of methylic and ethylic iodides on α-resorcylic acid, cresorcinol-, and quinol-carboxylic acids will be investigated.

An account is also given in this paper of the oximes of gallacetophenone, quinacetophenone, and resacetophenone. Digestion for a short time with acetic anhydride converts them into monacetyl derivatives.

EXPERIMENTAL.

Methylation of β-Resorcylic acid.

β-Resorcylic acid dissolved in a solution of the calculated quantity of sodium methoxide in methylic alcohol was treated with excess of methylic iodide, and the mixture boiled for 50 hours. After removing the unchanged methylic iodide, the product was poured into water, extracted with ether, and the extract, after being washed, first with water, and then with dilute sodium carbonate solution, was dried over calcium chloride and evaporated. The brown, syrupy residue thus obtained deposited crystals on standing; these were drained upon a porous tile and purified by several crystallisations from methylic alcohol.

0·1438 gave 0·3226 CO_2 and 0·0824 H_2O. $C = 61·18$; $H = 6·36$.

$C_{10}H_{12}O_4$ requires $C = 61·22$; $H = 6·12$ per cent.

It formed a beautiful, colourless mass of long, prismatic needles, melting at 76—77°, readily soluble in hot alcohol, but somewhat sparingly in light petroleum. It is insoluble in cold solutions of the alkali hydroxides. The methoxy-groups present were determined by Zeisel's method.

0·2274 gave 0·5430 AgI. $CH_3 = 15·24$.

$CH_3·C_6H_2(OCH_3)(OH)·COOCH_3$ requires $CH_3 = 15·30$ per cent.

It contained, therefore, but two methoxy-groups, of which one is present in the form of the methylic salt; it must therefore be considered to be a *monomethyl ether of the methylic salt of methyl-β-resorcylic acid.* As discussed in the introduction, its constitution is apparently $OCH_3 : OH : COOCH_3 = 1 : 3 : 4$. In order to obtain the acid from this methylic salt, it was first digested with boiling dilute alkali until a clear solution was obtained; the alkaline solution was then neutralised with acid, and the colourless precipitate collected, washed, and dried. It was purified by crystallisation from alcohol and toluene respectively.

0·1192 gave 0·2590 CO_2 and 0·0614 H_2O. C = 59·25; H = 5·72.
0·1094 gave, by Zeisel's method, 0·1487 AgI. CH_3 = 8·67.

$CH_3{\cdot}C_6H_2(OCH_3)(OH){\cdot}COOH$ requires C = 59·34; H = 5·49; CH_3 = 8·24 per cent. It was therefore a *monomethyl ether of methyl-β-resorcylic acid.*

Thus obtained, it formed colourless needles, melting at 210° with evolution of gas, this decomposition being evidently due to the splitting off of the carboxyl group, as is the case with β-resorcylic acid itself. The product consisted of a brownish oil, which, after standing for several days, became crystalline, but its examination was deferred until larger quantities could be obtained. It is readily soluble in alcohol, sparingly in water and toluene. With ferric chloride, an aqueous solution of the acid yields a claret-red coloration.

The alkaline washings of the ethereal extract obtained during the isolation of the above methylic salt were neutralised with acid, extracted with ether, and the extract evaporated. The nearly colourless, crystalline residue consisted chiefly of two substances, which were separated by fractional crystallisation from alcohol and dilute alcohol, a somewhat tedious process, the most insoluble product being obtained in colourless needles, melting at 210°, and the second, which had a similar appearance, melting at 151°.

The former, on examination, proved to be the monomethyl ether of methyl-β-resorcylic acid [$OCH_3 : OH : COOH = 1 : 3 : 4$] described above. A Zeisel's determination gave the following result.

0·4302 gave 0·5564 AgI. CH_3 = 8·25.
$CH_3{\cdot}C_6H_2{\cdot}(OCH_3)(OH){\cdot}COOH$ requires CH_3 = 8·24 per cent.

The second, or more soluble, substance, melting at 151°, was analysed, with the following result.

0·1370 gave 0·2900 CO_2 and 0·0645 H_2O. C = 57·73; H = 5·22.
0·2195 gave, by Zeisel's method, 0·3090 AgI. CH_3 = 8·98.

$OCH_3{\cdot}C_6H_3{\cdot}(OH){\cdot}COOH$ requires C = 57·14; H = 4·76; CH_3 = 8·92 per cent. It was evidently a *monomethyl ether of β-resorcylic acid.* Its properties agreed with those given for the methyl ether [$OCH_3 : OH : COOH = 1 : 3 : 4$] previously obtained by Tiemann and Parrisius (*loc. cit.*) by the methylation of β-resorcylic acid.

The original aqueous liquid remaining after the extraction of the mixed products of the methylation with ether was neutralised with acid, extracted with ether, and the extract evaporated. A dark brown, oily residue remained, from which nothing crystalline separated, even on long standing. It probably consisted of a mixture of methyl ethers of resorcinol, the latter being produced from the decomposition of some of the resorcylic acid in the earlier stages of the reaction.

Ethylation of β-Resorcylic acid.

The method employed in studying the action of ethylic iodide on β-resorcylic acid was similar to that previously described. The product was extracted with ether, the extract washed with dilute sodium carbonate solution, dried, and evaporated. The oily residue thus obtained deposited crystals, on standing, which were drained upon a porous tile and purified by several crystallisations from methylic alcohol.

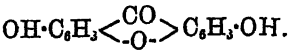
0·1123 gave 0·2578 CO_2 and 0·0690 H_2O. C = 62·60; H = 6·82.
$OEt{\cdot}C_6H_3(OH){\cdot}COOEt$ requires C = 62·85; H = 6·66 per cent.

It was obtained in long, colourless needles, melting at 53°, readily soluble in alcohol; cold alkali solutions dissolve it with difficulty.

In order to convert it into the acid, it was digested with a boiling solution of dilute caustic potash, until a clear solution was formed; this, when acidified, deposited a colourless precipitate, which was collected, washed, and purified by crystallisation from dilute alcohol.

0·1090 gave 0·2372 CO_2 and 0·0562 H_2O. C = 59·34; H = 5·72.
0·1964 gave, by Zeisel's method, 0·2575 AgI. C_2H_5 = 16·17.
$OEt{\cdot}C_6H_3(OH){\cdot}COOH$ requires C = 59·34; H = 5·49; C_2H_5 = 15·93 per cent.

β-Resorcylic acid monethyl ether forms colourless needles, melting at 153—154°, sparingly soluble in water, readily in alcohol. Its aqueous solution gives a claret-red coloration with ferric chloride.

Salicylic acid, when distilled with acetic anhydride, yields diphenylene ketone oxide, $C_6H_4<^{CO}_{O}>C_6H_4$, and β-resorcylic acid, by similar treatment, gives iso-euxanthone,  $OH\cdot C_6H_3<\overset{CO}{\underset{-O-}{}}>C_6H_3\cdot OH$. If the above ethyl ether have the constitution, OEt : OH : COOH = 1 : 3 : 4, iso-euxanthone diethyl ether should be produced from it by this reaction. In order to determine this point, a small portion of the substance was digested with acetic anhydride in a small retort and the product rapidly distilled. Towards the end of the operation a distillate was obtained, which solidified in the neck of the retort; this was collected, washed with a little alcohol, and recrystallised from the same solvent.

0·1203 gave 0·3150 CO_2 and 0·0574 H_2O. C = 71·41; H = 5·30.
$C_{17}H_{10}O_4$ requires C = 71·83; H = 5·63 per cent.

It appeared as a mass of nearly colourless needles, melting at 185°, moderately soluble in alcohol, but insoluble in alkaline solutions.

Experiment showed that the yield of this diethyl ether from the ethyl ether of β-resorcylic acid is considerably greater than that of iso-euxanthone from β-resorcylic acid itself.

From these results, it is evident that the ethylic salt of the ethyl ether of β-resorcylic acid and the free acid produced by its saponification have respectively the constitution, OEt : OH : COOEt and OEt : OH : COOH = 1 : 3 : 4.

The alkaline washings of the ethereal extract obtained during the isolation of the above ethylic salt, were neutralised with acid, extracted with ether, and the extract evaporated. The nearly colourless, crystalline residue consisted chiefly of a single substance, there being traces present, however, of a second more soluble product. By crystallisation from toluene, the latter was readily removed.

0·1142 gave 0·2493 CO_2 and 0·0590 H_2O. C = 59·53; H = 5·74.
0·1191 „ 0·2577 „ „ 0·0590 „ C = 59·01; H = 5·50.
$OEt\cdot C_6H_3(OH)\cdot COOH$ requires C = 59·34; H = 5·49 per cent.

It crystallised in colourless needles, melting at 153—154°, and is identical with the monethyl ether of β-resorcylic acid

[OEt : OH : COOH = 1 : 3 : 4]

above described. The quantity of the more soluble product accompanying it being small, its examination has been deferred.

Methylresacetophenone Monomethyl Ether.

Experiments were made on the methylation of resacetophenone, but, as stated in the introduction, the results obtained have been anticipated by others. The principal product of the reaction, which was insoluble in alkalis, crystallised in colourless leaflets, melting at 83—84°.

0·1812 gave 0·4450 CO_2 and 0·1345 H_2O. C = 66·96; H = 7·22.
0·1543 „ 0·3780 „ „ 0·0940 „ C = 66·81; H = 6·76.
$C_6H_2Me(OMe)(OH)\cdot CO\cdot CH_3$ requires C = 66·66; H = 6·66 per cent.

It possessed the above constitution, which has been previously assigned to it by G. Gregor (*loc. cit.*).

To investigate the action of bromine on this substance, it was dissolved in six times its weight of carbon bisulphide, and the solution treated gradually with sufficient bromine, dissolved in the same solvent, to form the monobrominated derivative. The action took place readily, and as soon as hydrobromic acid ceased to be evolved, the solution was evaporated, the residue spread upon a porous tile, and purified by several crystallisations from light petroleum.

0·3359 gave 0·2422 AgBr. Br = 30·69 per cent.
$C_6HBrMe(OMe)(OH)\cdot CO\cdot CH_3$ requires Br = 30·89 per cent.

It forms long, thin, colourless needles, melting at 63—64°, sparingly soluble in light petroleum. It is not attacked, even when digested with boiling alcoholic potash, and from this and other reactions it was shown to contain the bromine in the nucleus, and not in the side chain.

Preliminary experiments have also been carried out on the methylation of gallacetophenone, in a similar manner to those previously described with β-resorcylic acid. The chief product of the action crystallised in colourless needles melting at 77—78°.

0·1133 gave 0·2540 CO_2 and 0·0650 H_2O. C = 61·13; H = 6·37.
$C_6H_2(OH)(OCH_3)_2\cdot CO\cdot CH_3$ requires C = 61·22; H = 6·12 per cent.

It has therefore the composition of a dimethyl ether. I desire to reserve to myself the further study of this substance.

Oxime of Gallacetophenone.

Gallacetophenone (4 grams) dissolved in an aqueous solution of potash (14 grams) was treated with a solution of hydroxylamine hydrochloride (4 grams), rise in temperature being avoided. After standing 12 hours, the product was neutralised with acid, extracted with ether, and the extract evaporated; the brown, crystalline residue was purified first by crystallisation from water, and finally from toluene with the aid of animal charcoal.

0·3600 gave 24 c.c. moist nitrogen at 17°, and 743 mm. N = 7·56.
$C_6H_2(OH)_3\cdot C(NOH)\cdot CH_3$ requires N = 7·65 per cent.

It formed colourless needles, melting at 162—163°, and decomposing slightly above this temperature. Crystallisation of the crude product from water, in which it is sparingly soluble, does not render it colourless, benzene and toluene being the only useful solvents for this purpose. It dissolves readily in acetic anhydride, on gentle warming, but this solution, when raised to the boiling point, suddenly solidifies if concentrated, owing to the separation of crystals. These were collected, drained upon a porous tile, and purified by crystallisation from acetic acid.

0·1053 gave 0·2068 CO_2 and 0·0505 H_2O. C = 53·56; H = 5·32.
0·1677 „ 8·8 c.c. moist nitrogen at 20°, and 756 mm. N = 5·97.
$C_{10}H_{11}NO_5$ requires C = 53·33; H = 4·90; N = 6·22 per cent.

A determination of the acetic acid yielded by its decomposition with baryta water gave 28·19 per cent., the theory for one acetyl group being 28·09 per cent.; it was therefore a monacetyl derivative. From acetic acid, it crystallises in almost colourless needles, soluble in dilute alkalis. When heated, it commences to darken at 150—155°, and melts with rapid decomposition at 165°, gas being evolved, and if some quantity be melted, this action is so violent as to frequently give rise to a slight explosion; on digestion with solvents of high-boiling point, the same decomposition takes place, but more moderately, and it is hoped in this way to study the action.

The *oxime of resacetophenone* has been studied by Wechsler (*loc. cit.*), and, in order to investigate its behaviour with acetic anhydride, a small quantity was prepared; it readily dissolved, on gently warming, and when the solution was boiled for a few seconds and cooled rapidly, crystals separated. These were collected and purified by crystallisation from toluene.

0·1466 gave 7·7 c.c. moist nitrogen at 17°, and 766 mm. N = 6·14.
0·1423 „ 0·2995 CO_2 and 0·0730 H_2O. C = 57·40; H = 5·69.
$C_{10}H_{11}NO_4$ requires C = 57·41; H = 5·26; N = 6·6 per cent.

It was obtained as nearly colourless needles, readily soluble in acetic acid, soluble in alkalis. When heated, it melts and decomposes at 174—175°, but this action is not violent, as is the case with the gallacetophenone compound, gas being but gently evolved.

Oxime of Quinacetophenone.

This was prepared in a similar way to the gallacetophenone compound. The product was purified by crystallisation from water and toluene.

0·1894 gave 14·4 c.c. moist nitrogen at 18°, and 767 mm. N = 8·86.
$C_6H_3(OH)_2{\cdot}C(NOH){\cdot}CH_3$ requires N = 8·38 per cent.

It crystallises from toluene in colourless leaflets, melting at 149—150°.

When heated with acetic anhydride, it behaves similarly to resacetophenone oxime, a substance, apparently a monacetyl compound, being produced; this crystallises from benzene in colourless needles, soluble in alkalis, and melting with gentle decomposition at 146—147°.

In concluding this paper, I desire to express my thanks to Mr. W. R. Allen, a former student, for his assistance during the carrying out of a portion of this investigation.

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CII.—*Note on the Gravimetric Estimation of Maltose by Fehling's Solution.*

By T. A. Glendinning, F.I.C.

The alkaline copper solution originally devised by H. Fehling for the estimation of cupric-reducing sugars was prepared as follows (*Annalen*, **72**, 106, and **106**, 75). Forty grams of pure, crystallised copper sulphate dissolved in 160 grams of water. 160 grams of neutral potassium tartrate dissolved in a little water and mixed with 600—700 grams of caustic soda solution of sp. gr. 1·12; to this, the above solution of copper sulphate was gradually added, and the mixture diluted to 1154·4 c.c. at 15°. It was stipulated that the solution should be kept in well-filled, well-stoppered bottles, light being excluded to avoid decomposition.

At the present time, Fehling's solution used by chemists has practically the above composition, although it is now usual to mix the copper sulphate and alkaline tartrate solutions, when required; the tendency of Fehling's solution, which has been kept any length of time, to deposit cuprous oxide on heating is thus avoided.

The strength of the solution is such that 1,000 c.c. are exactly reduced by 5 grams of glucose; in other words, since 5 mols of cupric oxide are reduced by 1 mol. of glucose, each c.c. of such a solution contains 0·03464 gram of crystallised copper sulphate, or 34·64 grams per litre.

It has been repeatedly observed by the author that if potash in equivalent quantity is substituted for the soda in Fehling's solution, the cupric-reducing power of a solution containing maltose (wort, beer, malt-extract, &c.) always indicates a greater percentage of maltose than when soda is used; that is to say, the weight of cupric oxide reduced is greater in the former case than in the latter. The regularity with which this difference was exhibited under varying conditions could not be accidental, and experiments were therefore carried out to determine whether this is a constant and definite difference, which, up to now, has been overlooked.

Copper Sulphate Solution.—The "pure" commercial salt was recrystallised and a solution of it prepared, containing 69·28 grams per litre.

Rochelle Salt.—The salt usually supplied by the trade is impure, and requires careful recrystallisation. The readiest means of obtaining the pure substance is to add pure sodium carbonate to a strong solution of hydrogen potassium tartrate (cream of tartar) until slightly alkaline; on evaporation, the pure crystallised salt is easily obtained.

Alkaline Tartrate Solution.—For the soda solution, 360 grams of the purified Rochelle salt and 140 grams of caustic soda were dissolved in water and diluted to 1 litre.

For the potash solution, 360 grams of Rochelle salt and 196 grams of caustic potash (equivalent to 140 grams soda) were dissolved in water and diluted to 1 litre.

Fehling's solution was prepared, immediately before use, by mixing equal volumes of the copper sulphate solution and alkaline tartrate solution as required.

In all gravimetric determinations of cupric-reducing sugars, it is absolutely necessary, in order to obtain accurate and comparable results, to adhere strictly to the same conditions of experiment. In the following determinations, the dilution was so arranged that after adding the sugar solution, the total volume of the *diluted* Fehling's solution was 3¼ to 3½ times that of the *undiluted* Fehling's solution, and the precipitated cuprous oxide equivalent to 0·15 to 0·2 gram of CuO. After remaining for 11 to 12 minutes in the vigorously boiling water bath, the precipitated cuprous oxide was collected on a filter and weighed as CuO. Duplicate experiments were made, employing both asbestos tubes (Soxhlet's), with ignition in a current of oxygen, and also small double filter-papers, which were ignited in open crucibles. The amount of sugar solution used was always weighed and referred to its specific gravity to estimate the volume.

The Cupric Reducing Power of Maltose.

A specimen of maltose which had been purified by repeated crystallisations from water and from alcohol, until its opticity and cupric-reducing power were constant, yielded, as the result of a large number of estimations, the following.

	Cupric-reducing power.	
	$K_{3·86}$*.	Absolute.
Soda Fehling	61	62
Potash Fehling	64	65

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* For the meaning of this symbol see Brown and Heron, Trans., 1879, 35, 596.

The value given by O'Sullivan was $K_{3\cdot85} = 65$ (*J. Chem. Soc.*, 1876, **33**, 127), but this was subsequently corrected by him to $K_{3\cdot95} = 62\cdot5$ (Trans., 1884, **45**, 4), which is equivalent to $K_{3\cdot86} = 61$.

Brown and Heron (Trans., 1879, **35**, 596) determined this value to be $K_{3\cdot86} = 61$, which has been repeatedly confirmed by Brown and Morris in their communications to this Society since that date.

On applying the above results to the analyses of starch transformations, according to the definite lines laid down by Brown and Heron and by Brown and Morris, they were found to hold good in every case; thus—

A. *Starch Transformation at 60° C. with Cold Water Malt-extract of Air-dried Malt.*

$(\alpha)_{j\,3\cdot86} = 164\cdot0.$

With soda Fehling.		With potash Fehling.	
$K_{3\cdot86}$ 48·5		$K_{3\cdot86}$ 51·0	
Corresponding to—			
Maltose	79·5	Maltose	79·68
Dextrin	20·5	Dextrin	20·32
	100·0		100·00

Calculated :—

$(\alpha)_{j\,3\cdot86}$ 163·5. $(\alpha)_{j\,3\cdot86}$ 163·4.

B. *Starch Transformation with Cold Water Malt Extract, previously heated to* 66°.

$(\alpha)_{j\,3\cdot86}$ 167·8.

With soda Fehling.		With potash Fehling.	
$K_{3\cdot86}$ 43·8.		$K_{3\cdot86}$ 46·2.	
Corresponding to—			
Maltose	71·88	Maltose	72·18
Dextrin	28·12	Dextrin	27·82
	100·00		100·00

Calculated :—

$(\alpha)_{j\,3\cdot86}$ 168·5. $(\alpha)_{j\,3\cdot86}$ 168·3.

C. *Starch Transformation with Malt Extract previously heated to* 75°.

$(\alpha)_{j\,3\cdot86}$ 179·0.

With soda Fehling.	With potash Fehling.
$K_{3\cdot86}$ 33·84	$K_{3\cdot86}$ 35·68

Corresponding to—

Maltose	55·46	Maltose	55·75
Dextrin	44·54	Dextrin	44·25
	100·00		100·00

Calculated:—

$(\alpha)_{j3\cdot86}$ 179·4 $(\alpha)_{j3\cdot86}$ 179·2

The fact that some chemists are in the habit of using potash instead of soda for the preparation of Fehling's solution* is probably one of the reasons why discordant results are sometimes given by different authors as to the composition of solutions containing maltose, such as starch transformations. If, for example, in the above transformation C, the value of maltose be taken as 61, we should have, using potash Fehling,

$K_{3\cdot86}$ = 35·68, corresponding to

Maltose	58·5
Dextrin	41·5
	100·0

Calculated $(\alpha)_{j3\cdot86}$ 177·4°, instead of 179·0° actually observed.

The question naturally suggests itself, whether this difference in behaviour towards the two kinds of Fehling's solution is confined to maltose, or whether other sugars behave in a similar manner.

The other sugars so far examined are dextrose and invert sugar, but each is found to give identical results with soda and potash. It is noticeable that the cuprous oxide precipitated by maltose from potash Fehling is of a duller red, and does not separate as readily as when soda Fehling is used. The precipitate yielded by either solution has the same appearance, and separates with equal readiness, when precipitated by dextrose or invert sugar.

CIII.—*Studies in the Malonic Acid Series.*

By S. Ruhemann, Ph.D., M.A., and K. J. P. Orton, B.A., Hutchinson Student of St. John's College, Cambridge.

The halogen derivatives of malonic acid have been frequently subjected to close investigation, especially by Conrad and his pupils; this study led to the synthesis of polybasic acids and of a number of other interesting compounds. The readiness with which the bromine in the bromo-derivatives of malonic acid is displaced by other groups is also shown by some observations which we have made on dibromomalonamide. The action of nitric acid on malonamide resembles that of the halogens, in that it gives rise to the formation of nitromalonamide, and this can readily be transformed into amidomalonic acid which A. Baeyer (*Annalen*, **131**, 291) discovered in the course of his investigations in the uric series. An account of the above indicated research is contained in this communication, together with the result of our experiments on the action of hydrazine hydrate on ethylic ethoxymethylenemalonate; the latter was undertaken with a view of ascertaining whether hydrazine behaves towards this derivative of malonic acid in the same way as phenylhydrazine does (Claisen and Haase, *Ber.*, 1895, **28**, 35), yielding ethylic pyrazolonecarboxylate, which one of us obtained from ethylic dicarboxyglutaconate (*Ber.*, 1894, **27**, 1658).

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* Pavy ('Physiology of the Carbohydrates,' p. 68) strongly recommends potash instead of soda. See also Moritz and Morris ('Text Book of the Science of Brewing,' "Fehling's Solution," p. 517).

Diamidomalonamide.—On allowing dibromomalonamide, prepared according to Freund's directions (*Ber.*, 1884, **17**, 782), to remain in contact with a concentrated aqueous solution of ammonia for several days at the ordinary temperature, it is completely transformed into diamidomalonamide. The product, when collected and washed with alcohol, is free from bromine, and shows the characters of the compound which Conrad and Brückner (*Ber.*, 1891, **24**, 3002) obtained from ethylic dibromomalonate.* Its composition was verified by analysis of the product dried in a vacuum over sulphuric acid.

0·2158 gave 79·5 c.c. moist nitrogen at 16° and 746 mm. N = 42·13.

$C_3H_8O_2N_4$ requires N = 42·42 per cent.

Hydrazone of Mesoxalamide.—Hydrazine hydrate removes the halogen from dibromomalonamide, as does ammonia, with formation of the hydrazone of mesoxalamide. On adding the base to the dry amide, the action is so violent that it is advisable to dilute with alcohol; the action is completed by warming for a short time on the water bath. As the solution cools, it deposits long, colourless needles, which are somewhat soluble in cold but readily in boiling water, from which they can be recrystallised. The substance melts at 175°, gas being evolved. On analysis it gave numbers corresponding to the formula $(CONH_2)_2C{:}N{\cdot}NH_2$.

0·2240 gave 0·2300 CO_2 and 0·0912 H_2O. C = 27·84; H = 4·52.

0·2010 „ 75 c.c. moist nitrogen at 20° and 767 mm. N = 43·08.

$C_3H_6N_4O_2$ requires C = 27·70; H = 4·61; N = 43·07 per cent.

The *phenylhydrazone of mesoxalamide* is formed by heating an alcoholic solution of dibromomalonamide with the required quantity of phenylhydrazine on the water bath for about half an hour. The solution, on cooling, deposits long, yellow needles which are slightly soluble in cold and somewhat more readily in boiling alcohol. Glacial acetic acid, also, dissolves the substance, especially when boiling. It melts at 232—233°. A nitrogen determination agreed with the formula $(CO\cdot NH_2)_2C{:}N\cdot NH\cdot C_6H_5$.

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* We observed that the ethereal salt boils at 135—137° under a pressure of 13 mm., whilst, according to Conrad and Bruckner, it distils at 145—155° under a pressure of 25 mm.

0·1970 gave 45 c.c. moist nitrogen at 15° and 764 mm. N = 27·19.

$C_9H_{10}N_4O_2$ requires N = 27 18 per cent.

Bromine and nitric acid act on the phenylhydrazone of mesoxalamide, forming bromo- and nitro-derivatives. The former is obtained by adding an excess of bromine gradually to the hydrazone dissolved in warm glacial acetic acid; the yellowish-brown precipitate which separates is collected, washed with alcohol, and dissolved in boiling glacial acetic acid; canary-yellow needles, which melt at 240°, crystallise from it. The following analyses lead to the formula

$$(CO\cdot NH_2)_2C{:}N\cdot NH\cdot C_6H_4Br.$$

0·2950 gave 0·1973 AgBr. Br = 28·44.
0·2008 „ 34 c.c. moist nitrogen at 22° and 764 mm. N = 19 27.
0·1946 „ 33·8 c.c. „ 26° and 763 mm. N = 19·34.

$C_9H_9BrN_4O_2$ requires Br = 28·07; N = 19·64 per cent.

The nitrophenylhydrazone of mesoxalamide,

$$(CONH_2)_2C{:}N\cdot NH\cdot C_6H_4\cdot NO_2,$$

is prepared by adding fuming nitric acid carefully to a cold solution of the phenylhydrazone in glacial acetic acid; the deep yellow solution is poured on to ice, and the yellow precipitate produced, after being washed with water, is recrystallised from glacial acetic acid. It crystallises in yellow needles which decompose at 235°. On analysis the following numbers were obtained.

0·1988 gave 0·3126 CO_2 and 0·0682 H_2O. C = 42·88; H = 3·81.
0·2078 „ 50 c.c. moist nitrogen at 25° and 757 mm. N = 26·71.
0·1504 „ 36 c.c. „ 21° and 758 mm. N = 27·17.*

$C_9H_9N_5O_4$ requires C = 43·02; H = 3·59; N = 27·88 per cent.

The nitrophenylhydrazone of the mesoxalamide is readily decomposed by potash, producing a deep red solution, from which, on the addition of hydrochloric acid, a yellow substance is precipitated; this dissolves in glacial acetic acid, and separates from the solution in yellow needles, which decompose at 245°. This compound is most probably the phenylhydrazone of mesoxalic acid, formed by hydrolysis of the amide.

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* The percentage of nitrogen found by analysis in substances of this class is always lower than that required by the formula.

Nitromalonamide.—Franchimont and Klobbie (*Rec. Trav. Chim.*, 8, 283) have, in the course of their researches on the action of nitric acid on organic compounds, obtained the nitro-derivatives of methylic and ethylic malonate. We have found that the nitro-group can be introduced into malonamide with the same readiness as bromine. The nitromalonamide is prepared by very gradually adding one part of malonamide to eight parts of fuming nitric acid. During the addition of the malonamide to the acid, the mixture must be kept cold by ice and well stirred. The separation of the nitromalonamide begins before the whole of the malonamide is introduced. The product is poured on to ice; the nitromalonamide is collected and washed thoroughly with cold water, in which it is almost insoluble. The amide thus obtained dissolves in boiling water, and, on cooling, separates in six-sided prisms, which decompose at 172°. Analysis confirms the formula $CH(NO_2)(CONH_2)_2$.

0·2104 gave 0·1874 CO_2 and 0·0672 H_2O. C = 24·29; H = 3·54.
0 1758 „ 44·5 c.c. moist nitrogen at 25° and 768 mm. N = 28·54.
$C_3H_5N_3O_4$ requires C = 24 48. H = 3·40. N = 28·57 per cent.

Nitromalonamide has acid properties, as have the ethereal salts of nitromalonic acid (Franchimont and Klobbie, *loc. cit.*). The potassium derivative is prepared by dissolving the nitromalonamide in pure dilute potash, and is precipitated from the solution on adding absolute alcohol, in the form of colourless needles which dissolve readily in water forming a yellow solution. For analysis, the salt was dried in a vacuum over sulphuric acid and finally at 100°.

0·3126 gave 0·1442 K_2SO_4. K = 20·68.
0 3098 „ 0·1436 K_2SO_4. K = 20·78.
$C_3H_4KN_3O_4$ requires K = 21·08 per cent.

The silver derivative is prepared from the aqueous solution of the potassium compound by adding silver nitrate; it gradually separates in colourless prisms which dissolve in boiling water. It was dried in a vacuum over sulphuric acid, and then at 100°.

0·3778 gave 0·1604 Ag. Ag = 42·45.
$C_3H_4AgN_3O_4$ requires Ag = 42·52 per cent.

The lead salt is deposited in yellow, rhombic crystals on mixing solutions of the potassium salt and lead acetate.

0·3176 gave 0·1920 $PbSO_4$. Pb = 41·30.
$(C_3H_4N_3O_4)_2Pb$ requires Pb = 41·48 per cent.

Nitromalonamide dissolves readily in ammonia, and the salt is precipitated from the aqueous solution by alcohol in colourless needles.

An attempt was made to prepare methylnitromalonamide from the silver salt. Methylic iodide does not act on the silver salt when they are heated together on the water bath; an action, however, takes place on digesting it with methylic iodide in the presence of methylic alcohol in a sealed tube at 100° for two or three hours. A gas escaped on opening the tube; the latter contained, besides silver iodide, colourless crystals suspended in the liquid. The solid was collected and extracted with boiling water, which, on cooling, deposited colourless plates melting at 173—174°. The melting point and crystalline form of this substance as well as a nitrogen determination proved it to be nitromalonamide.

0·1604 gave 40 c.c. moist nitrogen at 21° and 759 mm. N = 28·34.
$C_3H_5N_3O_4$ requires N = 28·57 per cent.

The formation of nitromalonamide from the silver salt is most probably explained by assuming an interaction to occur between the methylic iodide and methylic alcohol which produces methylic ether and hydrogen iodide, the latter decomposing the silver salt.

Action of Aniline on Nitromalonamide.

When nitromalonamide is warmed with excess of potash or baryta, decomposition immediately takes place, and ammonia is evolved. The salts of nitromalonic acid, however, were not obtained, for on boiling until ammonia ceased to come off, it was found that decomposition had taken place, potassium or barium carbonate having been formed.

Nitromalonamide is also decomposed on heating it with aniline; on boiling the amide with the base in a flask fitted with a reflux condenser, it enters into solution, ammonia is evolved, and the contents of the flask darken; when cold, the liquid solidifies almost completely to a mass of coloured crystals, which dissolve in hot alcohol and crystallise from the decolorised solution in colourless needles. The melting point (235°) and the chemical behaviour characterise this compound as diphenylcarbamide. A nitrogen determination gave the following result.

0·1792 gave 21 c.c. moist nitrogen at 22° and 758 mm. N = 13·23.
$C_{13}H_{12}N_2O$ requires N = 13·21 per cent.

Amidomalonic acid.—Amidomalonic acid was discovered by Baeyer (*Annalen*, **131**, 291), who obtained it by reducing nitrosomalonic acid, the product of the action of potash on violuric acid (nitrosobarbituric acid). Since nitromalonamide can be so readily prepared from malonic acid, it seemed to be of interest to subject this nitro-derivative to the action of reducing agents with a view of obtaining amidomalonic acid. The reduction is effected in the following manner:—Nitromalonamide is suspended in water and the calculated quantity of sodium amalgam, containing 2½ per cent. of sodium, is gradually introduced, the mixture being cooled with ice. The yellow colour of the solution of the sodium nitromalonamide slowly disappears, and the reduction is completed by adding a slight excess of sodium amalgam and heating on the water bath for half an hour. The alkaline solution is poured off from the mercury and boiled until ammonia, which first appeared during the reduction, ceases to be evolved. The cooled liquid is filtered and acidified with acetic acid; and, following Baeyer's directions, the amidomalonic acid is precipitated as lead salt by the addition of lead acetate. The acid is prepared by decomposing the lead salt, suspended in water, by hydrogen sulphide, filtering, and evaporating the filtrate from the lead sulphide in a vacuum over sulphuric acid, or by distilling it in a vacuum at a temperature of 50—55°. The colourless transparent prisms thus obtained melt at 109°, evolving carbon dioxide. A nitrogen determination of an air-dried specimen gave the following result.

0·2340 gave 21·5 c.c. moist nitrogen at 24° and 755 mm. N = 10·23.
$C_3H_5NO_4,H_2O$ requires N = 10·21 per cent.

The water of crystallisation is only very slowly given off in a vacuum over sulphuric acid.

Several salts of this acid have been prepared and analysed. The lead salt is obtained as described above, and, on analysis, gave numbers corresponding to the formula previously established by Baeyer, $[C_3H_2(NH_2)O_4]_2Pb$.

0·3824 gave 0·2624 $PbSO_4$. Pb = 46·88.
0·2236 „ 0·1534 $PbSO_4$. Pb = 46·87.
$C_6H_8N_2O_8Pb$ requires Pb = 46·72 per cent.

The silver salt precipitated on adding silver nitrate to the ammoniacal solution of the acid darkens under the influence of light. For analysis it was washed with alcohol, and dried in a vacuum.

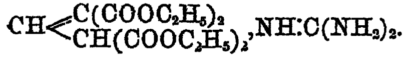
0·2014 gave 0·1304 Ag. Ag = 64·75.
$C_3H_3Ag_2NO_4$ requires Ag = 64·86 per cent.

The ammonium salt is precipitated by alcohol from its aqueous solution in colourless crystals; it is most probably the normal salt which, however, on drying at 100°, loses ammonia and yields the acid ammonium salt.

0·1616 gave 29 c.c. moist nitrogen at 22° and 757 mm. N = 20·22.
0·1752 „ 31·5 c.c. „ „ 21° and 756 mm. N = 20·34.
$C_3H_2(NH_2)O_4{\cdot}NH_4$ requires N = 20·58 per cent.

In connection with the experiments described above, we may here record the result of an investigation, in continuation of a research on the action of bases on ethylic dicarboxyglutaconate. It has already been shown by one of us, that ammonia and primary monamines and diamines of both the fatty and aromatic series act on the ethereal salt, forming ethylic amidoethylenedicarboxylate (ethylic amidomethylenemalonate) or its derivatives on the one hand, and the amide of malonic acid or the substituted amides on the other. It seemed to us of interest to subject ethylic dicarboxyglutaconate to the action of guanidine, in order to ascertain if, in this case also, a similar change would take place. We found, however, to our surprise, that such is not the case, but that it leads only to the formation of the guanidine salt of ethylic dicarboxyglutaconate.

On warming the ethereal salt with guanidine carbonate, dissolved in water, a solid is obtained, which is most probably a compound of both substances. This, on boiling with water, dissolves with evolution of carbon dioxide, and, on cooling, yellow prisms crystallise out; these melt and decompose at 163°. The fact that this compound is decomposed by hydrochloric acid with the formation of ethylic dicarboxyglutaconate and guanidine hydrochloride, shows it to be the guanidine salt of ethylic dicarboxyglutaconate, as does the analysis, which gives results corresponding with the formula



$$CH{<}\begin{matrix}C(COOC_2H_5)_2\\CH(COOC_2H_5)_2\end{matrix},NH{:}C(NH_2)_2.$$

0·2092 gave 0·3790 CO_2 and 0·1304 H_2O. C = 49·40; H = 6·92.

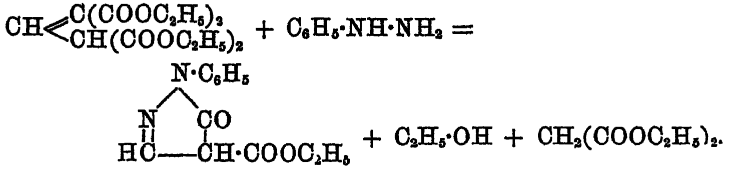
0·2040 „ 19·5 c.c. moist nitrogen at 20° and 755 mm. N = 10·86.

$C_{16}H_{27}N_3O_6$ requires C = 49·36; H = 6·94; N = 10·80 per cent.

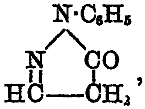
The same salt is formed when guanidine itself is used instead of the carbonate. The base is obtained by dissolving guanidine hydrochloride in absolute alcohol, and adding the calculated quantity of sodium dissolved in alcohol; the filtrate from the sodium chloride is evaporated in a vacuum, and the remaining guanidine mixed with ethylic dicarboxyglutaconate. Combination takes place immediately with evolution of heat, and the mixture solidifies to a mass of yellow crystals, which are identical with the product formed when guanidine carbonate is used.

Action of Hydrazine Hydrate on Ethylic Ethoxymethylenemalonate.

Ethylic dicarboxyglutaconate suffers, under the influence of phenylhydrazine, a decomposition similar to that which takes place with ammonia (Ruhemann and Morrell, Trans., 1892, 61, 793). This reaction gives rise to the formation of ethylic 1-phenyl-5-pyrazolone-4-carboxylate, and is represented by the equation

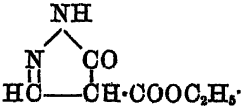


Claisen and Haase (*Ber.*, 1895, **28**, 35) have found lately that the same compound is also formed by the action of phenylhydrazine on ethylic ethoxymethylenemalonate. They concluded from the chemical behaviour of the phenylpyrazolone, formed from the ethylic pyrazolonecarboxylate, that it has the formula



and not the tautomeric formula which follows from its synthesis.

The action of hydrazine hydrate on ethylic dicarboxyglutaconate is like that of phenylhydrazine, yielding, as one of us has shown, ethylic pyrazolonecarboxylate, the constitution of which, in the light of Claisen and Haase's work, is to be represented by the formula



So close is the analogy between the mode of formation of this compound and its phenyl derivative, and also between the chemical behaviour of these substances, that it was scarcely to be expected that objections would be raised against the above formula. Such objections, however, have been brought forward by v. Rothenburg (*J. pr. Chem.*, 1894, **50**, 230), who has expressed the view that the action of hydrazine hydrate on ethylic dicarboxyglutaconate does not produce a pyrazolone derivative, but gives rise to a compound of double the molecular weight.

S. Ruhemann and R. S. Morrell (*Ber.*, 1895, **28**, 988) have shown that the molecular weight corresponds with that required by ethylic pyrazolonecarboxylate, $C_6H_8N_2O_3$. This formula is further supported by the following experiments which we were enabled to carry out by the kindness* of Professor Claisen, who allowed us to study the action of hydrazine hydrate on ethylic ethoxymethylenemalonate.

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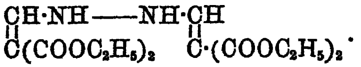
* I take this opportunity of expressing my thanks to Professor Claisen for not

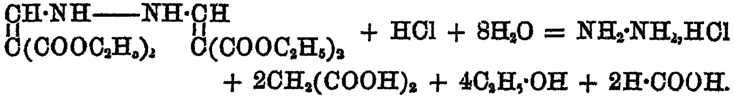
Hydrazine hydrate acts on ethylic ethoxymethylenemalonate as readily as phenylhydrazine does. The two substances, in molecular proportion, are gradually mixed in a flask, cooled by ice. They interact, and heat is evolved, a thick, yellow oil being formed, which solidifies slowly on standing; on washing the solid with dilute hydrochloric acid, it loses its yellow colour. The product readily dissolves in alcohol and ether, and crystallises from dilute spirit in colourless, rhombic prisms; it melts at 82° to a colourless oil, which only very slowly solidifies again. Analysis of the substance, dried in a vacuum over sulphuric acid, leads to the formula



$$\begin{matrix}\mathrm{CH{\cdot}NH} & \text{——} & \mathrm{NH{\cdot}CH} \\ \| & & \| \\ \mathrm{C(COOC_2H_5)_2} & & \mathrm{C{\cdot}(COOC_2H_5)_2}\end{matrix}\,.$$

0·2106 gave 0·3984 CO_2 and 0·1220 H_2O. C = 51·59; H = 6·41.
0·2152 „ 14 c.c. moist nitrogen at 17° and 770 mm. N = 7·75.
$C_{16}H_{24}N_2O_8$ requires C = 51 61; H = 6·45; N = 7·52 per cent.

The action of hydrazine hydrate on ethylic ethoxymethylenemalonate differs, therefore, from that of phenylhydrazine (Claisen and Haase, *loc. cit.*), yielding a compound, which may be regarded as the ethereal salt of hydrazodimethylenedimalonic acid. This view of the constitution is confirmed by its behaviour towards boiling hydrochloric acid. On heating the hydrazo-compound with the acid, it dissolves, and on evaporating the solution on the water bath, a crystalline residue is left, consisting of malonic acid and hydrazine hydrochloride. Their separation may be effected by means of ether, which dissolves the acid; on evaporating, and recrystallising the malonic acid from water, it melts at 132°. The part insoluble in ether was proved to be hydrazine hydrochloride by its chemical behaviour. The decomposition, which the hydrazo-compound suffers under the influence of hydrochloric acid may, therefore, be represented by the equation



$$\begin{matrix}\mathrm{CH{\cdot}NH} & \text{——} & \mathrm{NH{\cdot}CH} \\ \| & & \| \\ \mathrm{C(COOC_2H_5)_2} & & \mathrm{C(COOC_2H_5)_2}\end{matrix} + \mathrm{HCl} + 8\mathrm{H_2O} = \mathrm{NH_2{\cdot}NH_2,HCl}$$
$$+ 2\mathrm{CH_2(COOH)_2} + 4\mathrm{C_2H_5{\cdot}OH} + 2\mathrm{H{\cdot}COOH}.$$

The hydrazo-compound has acid properties, and, with alkalis, forms yellow salts. The sodium salt is readily obtained in the form of yellow needles by mixing alcoholic solutions of sodium ethoxide and the ethereal salt; the solution of the salt in water is strongly alkaline to litmus paper. For analysis, it was washed with alcohol, in which it is fairly soluble, and dried first in a vacuum over sulphuric acid, and finally at 100°.

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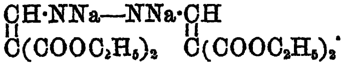
only allowing me to study this action, but also for furnishing me with the exact details of the preparation of ethylic ethoxymethylenemalonate.—S. R.

0·2062 gave 0·0680 Na_2SO_4. Na = 10·93.
0·2214 „ 0·0748 Na_2SO_4. Na = 10·94.
$C_{16}H_{22}Na_2N_2O_8$ requires Na = 11·05 per cent.

The sodium salt is, no doubt, formed by the displacement of the imidohydrogen atoms, and its constitution may be represented by the formula



$$\begin{matrix}\mathrm{CH\cdot NNa}- & \mathrm{NNa\cdot CH}\\ \| & \| \\ \mathrm{C(COOC_2H_5)_2} & \mathrm{C(COOC_2H_5)_2}\end{matrix}.$$

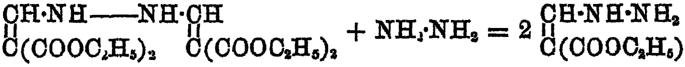
This constitution is in agreement with the behaviour of the hydrazo-compound towards hydrazine hydrate and ammonia. Under the influence of these agents, it suffers a remarkable decomposition, yielding ethylic pyrazolonecarboxylate.

Action of Hydrazine Hydrate on Ethylic Hydrazodimethylenedimalonate.

On adding an excess of hydrazine hydrate to the hydrazo-compound, heat is evolved, and a yellow solid is obtained, which is, no doubt, the hydrazine salt of ethylic hydrazodimethylenedimalonate; this is decomposed on warming on the water bath for a short time, yielding a colourless substance, which enters into solution. Hydrochloric acid precipitates from this solution colourless needles, which, after recrystallisation from water, melt at 180°; the properties of this product fully characterise it as ethylic pyrazolonecarboxylate, which has been obtained by the action of hydrazine hydrate on ethylic dicarboxyglutaconate (Ruhemann, *Ber.*, 1894, **27**, 1659), and on ethylic amidoethylenedicarboxylate (Ruhemann and Morrell, *Ber.*, 1894, **27**, 2747). The formula, $C_6H_8N_2O_3$, was, moreover, verified by a nitrogen determination of the substance dried at 100°.

0·2102 gave 33·5 c.c. of moist nitrogen at 25° and 764 mm. N = 17·86.
$C_6H_8N_2O_3$ requires N = 17·94 per cent.

The formation of the pyrazolone derivative in the above action may be explained by assuming that, under the influence of hydrazine hydrate, the hydrazo-compound undergoes a decomposition similar to that which takes place in the case of ethylic dicarboxyglutaconate. The transformation may be represented by the following equation.



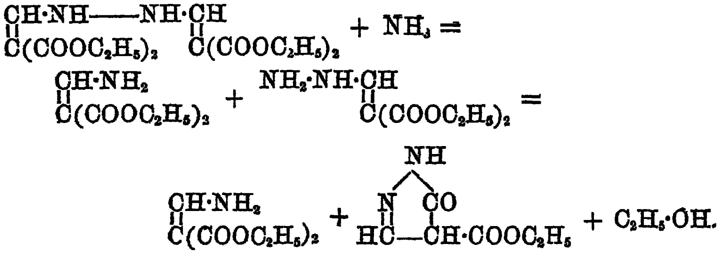
$$\begin{matrix}\mathrm{CH\cdot NH}- & \mathrm{NH\cdot CH}\\ \| & \| \\ \mathrm{C(COOC_2H_5)_2} & \mathrm{C(COOC_2H_5)_2}\end{matrix} + \mathrm{NH_2\cdot NH_2} = 2\begin{matrix}\mathrm{CH\cdot NH\cdot NH_2}\\ \| \\ \mathrm{C(COOC_2H_5)_2}\end{matrix}.$$

The ethereal salt of hydrazomethylenemalonic acid then loses alcohol and yields ethylic pyrazolonecarboxylate, which combines with hydrazine to form a salt. This salt has been obtained (Ruhemann, *Ber.*, 1894, **27**, 1659) from the product of the action of hydrazine on ethylic dicarboxyglutaconate. On adding hydrochloric acid, it is converted into ethylic pyrazolonecarboxylate.

The following experiment proves the correctness of the above view of the formation of the pyrazolone derivative from the hydrazo-compound.

Action of Ammonia on Ethylic Hydrazodimethylenedimalonate.

The explanation of the action mentioned above suggested that ammonia would effect a decomposition of the hydrazo-compound analogous to that which is brought about by hydrazine, which is expressed by the equation.



$$\begin{matrix}\mathrm{CH{\cdot}NH{-\!-}NH{\cdot}CH} \\ \| \qquad\qquad \| \\ \mathrm{C(COOC_2H_5)_2 \quad C(COOC_2H_5)_2}\end{matrix} + NH_3 = \begin{matrix}\mathrm{CH{\cdot}NH_2} \\ \| \\ \mathrm{C(COOC_2H_5)_2}\end{matrix} + \begin{matrix}\mathrm{NH_2{\cdot}NH{\cdot}CH} \\ \| \\ \mathrm{C(COOC_2H_5)_2}\end{matrix} =$$

Such a decomposition does, indeed, take place, and leads to the formation of ethylic pyrazolonecarboxylate and ethylic amidoethylenedicarboxylate. This transformation is effected by warming the hydrazo-compound with ammonia for about half an hour; the yellow salt, which is first produced, enters into solution, but after a short time an oil separates; this is taken up by ether, and crystallises from the decolorised solution in colourless needles. These were identified as ethylic amidoethylenedicarboxylate, which has been obtained together with malonamide by the action of ammonia on ethylic dicarboxyglutaconate (Ruhemann and Morrell, Trans., 1886, **49**, 745). The formula of this product was confirmed by a nitrogen determination.

0·2286 gave 15·5 c.c. of moist nitrogen at 25° and 765 mm. N = 7·61.
$C_8H_{13}NO_4$ requires N = 7·49 per cent.

The ammoniacal solution of the product, after being freed from ethylic amidoethylenedicarboxylate by extraction with ether, contains the ammonium salt of ethylic pyrazolonecarboxylate, and, on adding hydrochloric acid, yields a precipitate. This crystallises from water in colourless needles, and was identified as ethylic pyrazolonecarboxylate by the melting point (180°) and by a nitrogen determination.

0·2092 gave 32·5 c.c. moist nitrogen at 21° and 765 mm. N = 17·80.
$C_6H_8N_2O_3$ requires N = 17·94 per cent.

The result of this investigation, therefore, affords further confirmation of the correctness of the view, already expressed, concerning the constitution of the compound formed from hydrazine and ethylic dicarboxyglutaconate, namely, that it is ethylic pyrazolonecarboxylate. These experiments suffice to prove that the objections raised by v. Rothenburg are unfounded; a further discussion of his remarks appears to be unnecessary and undesirable. What is the relation of the result of the investigation recorded above to v. Rothenburg's pyrazolone? V. Rothenburg has put this question (*J. pr. Chem.*, 1894, **50**, 230); it is to be hoped that he will give a satisfactory answer.

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Cambridge.

CIV.—*Mercury Perchlorates.*

By Masumi Chikashigé, B.Sc.

Having, at the suggestion of Dr. Divers, prepared mercuric and mercurous perchlorates, with the object of examining their behaviour when heated, I found that their properties were not quite the same as those described by Serullas, and by Roscoe (*Proc. Roy. Soc.*, 1862, **11**, 502, and *Liebig's Annalen*, 1862, **121**, 346). The earlier memoir, which appeared in 1830 (*Ann. Chim. Phys.*, [2], **45**, 270), I have not seen, and my statements as to its contents are on the authority of the larger works on chemistry.

Most of the hydrated perchloric acid, used in my experiments, was prepared, as Roscoe directs, by treating potassium chlorate with hydrofluosilicic acid, but some of it by the more convenient process of precipitating barium chlorate with sulphuric acid. Although not mentioned by Roscoe, it is tolerably well known that the hydrated acid is slightly decomposed when it is distilled, becoming contaminated with chlorine and hydrochloric acid. I find, however, that the distilled acid can be easily freed from these impurities by heating it for a short time in the air.

Mercuric Perchlorate.

Mercuric perchlorate is formed when mercuric oxide is triturated with aqueous perchloric acid until the solution begins to grow turbid from the presence of basic salt; it is then filtered, preferably through asbestos, mixed with a few drops of perchloric acid, and concentrated at a gentle heat. Evaporation is then continued over sulphuric acid at the ordinary temperature until the salt crystallises. If necessary, it may be recrystallised, dissolving it in a very little water. It is quite stable, but needs some care to dry it, for it slowly effloresces in a desiccator, whilst in the air it very quickly deliquesces (Serullas), and a slight rise of temperature causes it to melt. Preserved for a day or two in bottles, however, its upper layers become dry by draining, and may then be quickly pressed between folds of paper.

Mercuric perchlorate crystallises in slender rectangular prisms, as described by Serullas, but being exceedingly soluble in water, as well as very hygroscopic, its slender crystals rapidly liquefy when exposed to the air. It reddens litmus (Serullas), but its freedom from acid can be shown by adding excess of sodium chloride to its solution, which renders it neutral. It shows a slight tendency to decompose with water, and in absence of any excess of acid, its solution deposits basic salt if evaporated by the aid of heat. Moreover, its slow efflorescence in the desiccator is the result of loss of acid as well as of water; so that the effloresced salt leaves some insoluble basic salt when dissolved in water.

Alcohol decomposes it still more easily. The effect of this agent has been described by Serullas. I find that alcohol at once decomposes the crystals of the salt, leaving a white basic salt undissolved; this again is decomposed by water which leaves impure mercuric oxide. Alcohol, also, added to an aqueous solution of mercuric perchlorate, gives an orange precipitate, mainly mercuric oxide. As to the formation of mercurous oxide or mercurous salt, which is mentioned in the handbooks as taking place on evaporating the mother liquor, that happens to a small extent only, and because mercuric salts are reduced by hot alcohol.

Of the composition of mercuric perchlorate all that is known is that, on the authority of Serullas, it is expressed by $Ag(ClO_4)_2$; it passes for an anhydrous salt (Roscoe and Schorlemmer's *Treatise*, Muir and Morley's *Watt's Dictionary*, &c.). It is, however, a hydrated salt, with as much as $6H_2O$, which, though it can be readily removed from the salt by heat, cannot well be directly estimated, since perchloric acid is liberated along with it from the first. The composition of the salt was determined by precipitating the mercury as sulphide and obtaining the perchloric acid from the filtrate as its potassium salt, with the precautions given in Roscoe's paper. The formation of a very little sulphuric acid in removing the excess of hydrogen sulphide, cannot be avoided, and this comes out in the potassium perchlorate and, small as it is, has to be taken into account. In the second of the analyses here given, the mercury was precipitated by gaseous hydrogen sulphide without addition of acid; in the first, it was precipitated by adding, at once, excess of hydrogen sulphide solution, and then 1 c.c of dilute sulphuric acid to aggregate the mercury sulphide. The total sulphuric acid having been determined, the corresponding quantity of potassium sulphate was deducted from that of the potassium perchlorate and sulphate together. In consequence of what has just been stated, this procedure introduced no complication, while the use of hydrochloric acid was precluded, as interfering with the determination of the perchloric acid. The calculation is for $Hg(ClO_4)_2,6H_2O$.

	Calc.	I.	II.
Mercury.............	39·45	39·26	38·95
Perchlorate radicle....	39·25	38·90	38·82
Water..............	21·30	—	—

Behaviour of Mercuric Perchlorate when Heated.—Mercuric perchlorate, as dry as possible, melts at about 34° in dry air. Heated in a long, narrow tube, closed only at its lower end, the salt melts to a colourless liquid, which boils freely, without noticeable change, even in a bath of boiling sulphur. In reality it is decomposed, and at temperatures far below this, but since the products of its decomposition, which boil off, condense and flow down again, the salt is recovered when the tube is cooled.

Even at the common temperature, as already mentioned, mercuric perchlorate very slowly decomposes in dry air, but in a current of dried air at 120°, the evolution of water and perchloric acid becomes manifest in the shape of white fumes. By raising the temperature gradually, and then maintaining it at 150° until the weight of the residue becomes constant, a homogeneous, and apparently definite compound is left. This compound, *oxymercuric perchlorate*, is white and amorphous; it is not changed by the heat of boiling mercury, and only slowly affected by that of boiling sulphur. Heated to a point a little below that at which mercuric oxide freely decomposes, it is completely changed into oxygen and chlorine gases, sublimates of mercuric and mercurous chlorides, and a residue of mercuric oxide. By water it is decomposed into mercuric perchlorate and mercuric oxide, besides insignificant quantities only of chloride and chlorate. In a quantitative experiment, it was found to yield to water, mercury 12·64, and perchlorate radicle, 12·90 per cent. of the original weight of the salt heated. Therefore, water dissolves out normal mercuric perchlorate, and, since 12·90 is almost exactly the third part of 39·25, the percentage amount of perchlorate radicle in the original salt, and the change effected by heat, may be formulated thus,

$$3[Hg(ClO_4)_2,6H_2O] = O_2Hg_3(ClO_4)_2 + 4HClO_4 + 16H_2O,$$

$O_2Hg_3(ClO_4)_2$ expressing the composition of the oxymercuric perchlorate.

Mercurous Perchlorate.

Mercurous perchlorate can be very quickly prepared by violently shaking a solution of mercuric perchlorate with mercury for a few minutes, after which nothing but the mercurous salt will be found in the solution. Such a solution cannot be left for days, or heated long on a water bath, without some basic salt being deposited, but a concentrated solution can be evaporated in a vacuum desiccator fast enough to avoid this. With rapid evaporation, the salt is obtained in fine needles, as described by Serullas; these are flat, and, with slower evaporation, develop into flattened prisms or plates of considerable size. The salt is exceedingly soluble in water, and causes a sensible fall in temperature in dissolving, the solution being neutral to litmus; with a large quantity of water, it is often decomposed. Serullas found the salt to be unchanged by exposure to air, and must therefore have been working in very dry weather, for it is, as Roscoe states, very deliquescent, though less so than the mercuric salt. According to Roscoe, it does not lose water, either at 100°, or in a vacuum over sulphuric acid; but this is not really the case, although the loss of weight is slow enough to be easily overlooked; when kept for about two weeks in a vacuum desiccator, the loss reaches nearly 6 per cent., and then ceases. This loss, though mainly that of water, includes also that of a little acid; a loss of half its water would amount to 5·36 per cent. of its weight. At 100°, in a current of dry air, it loses about 2 per cent. of water in six hours, a mere trace of acid also escaping, as was proved by placing litmus paper in the issuing current of air: in another six hours, it loses about 2 per cent. more in weight, including now a notable amount of acid.

As already stated, the salt is gradually decomposed by water; and when the white, basic salt thus produced is washed with water, it becomes black from loss of acid. Alcohol decomposes the solid salt into soluble acid salt and white basic salt, which is also blackened by washing with water, but not by alcohol. Alcohol added to an aqueous solution of the salt has no immediate effect.

In analysing the salt, the perchloric acid was determined in the same way as in the case of the mercuric salt, after removal of the mercury as sulphide, whilst the mercury was estimated in a separate portion of the salt by precipitation as mercurous chloride. The composition of the salt has been given by Roscoe as $(HgClO_4)_2,6H_2O$, he having found the mercury to be 56·60 per cent. as required by that formula. I have assured myself, however, by examining different preparations, that the crystals I obtained only contained 4 mols. water when not visibly moist, the formula being $(HgClO_4)_2,4H_2O$.

	Calc	I.	II.	III.	IV.
Mercury.........	59·61	59·00	58·90	—	—
Perchlorate radicle	29·66	—	—	29·60	29·50
Water...........	10·73	—	—	—	—

It might seem from our respective results that we had examined different hydrates, but in the several preparations I made of the salt, I never met with but one form of crystal which, with rapid evaporation in the vacuum desiccator, was that of fine needles, as described by Serullas and as got by Roscoe presumably, for he makes no mention at all of the form of his crystals. By somewhat slower evaporation in the desiccator, much larger crystals were obtained, and these were found to be preferable for analysis as they were more easily freed from mother liquor. For analysis, however, I used the fine needles as well as the plates. Of the three samples analysed, marked above II, III, IV, one consisted of fine needles that had formed the first crop, whilst the other two were larger crystals of the second crop from the same preparation; sample I was another preparation. If Roscoe's salt were a higher hydrate than that I obtained, it could not have been heated at 100°, even for a short time, or exposed to the dry air of a desiccator without loss, as he found it to do.

Behaviour of Mercurous Perchlorate when Heated.—Mercurous perchlorate, unlike the mercuric salt, has no melting point. Quickly raised to about 190°, the salt becomes partly liquid for a short time, but only from the presence of unvolatilised acid along with basic salt; when gradually heated, the salt does not show even this false fusion. At 100°, the crystals of the salt decrepitate; but it loses acid only very slowly at this temperature, and is still completely soluble in a little water, even after two or three hours' heating in an open tube. At about 150°, the crystals slowly intumesce and become opaque, basic salt being formed and also a little mercuric salt and a trace of chloride. Heated at 170° for some hours, its decomposition goes further; more mercuric salt is formed and a good quantity of chloride, as well as some chlorate (detected by decomposing with hydrochloric acid), whilst at 200° white fumes escape containing mercuric chloride. The more the salt is heated, the more basic it becomes, the redder and the larger is the residue left on treating it with water, and the less mercurous nitrate this residue yields when dissolved in nitric acid. Heated to 357° it suffers no further change, but at 444° decomposes slowly. The products are then the same as those found on heating the residue from the mercuric salt, but only very little free chlorine can be detected; metallic mercury does not occur among the products.

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CV.—α-Ethylene-Dihydroxylamine Dihydrobromide.

By C. M. LUXMOORE, D.Sc.

SEVERAL interesting substituted hydroxylamines having been recently obtained by the interaction of hydroxylamine and alkyl iodides, I have, at Professor Dunstan's suggestion, endeavoured to obtain derivatives containing two hydroxylamine residues in the molecule. I have only succeeded so far in preparing one such compound, but as the work has been interrupted, it seemed desirable to communicate to the Society the results obtained.

Ethylenic bromide does not react with hydroxylamine hydrochloride when the two are heated in alcoholic solution at 110—115°, but if a solution of hydroxylamine, obtained by adding to a solution of the hydrochloride in methylic alcohol slightly less than the calculated quantity of sodium methoxide, is heated with ethylenic bromide at 95—100°, for a couple of hours, and the alcohol then distilled off, a white crystalline residue is left, which can be purified by recrystallisation from alcohol and ether. This substance is soluble in water and in alcohol, but insoluble in ether. When heated, it does not melt below 250°, and above that temperature it darkens and chars.

A bromine determination gave the following data.

0·2422 gave 0·3608 AgBr. Br = 63·3.

$C_2H_{10}N_2O_2Br_2$ requires Br = 63 per cent.

The substance is therefore formed according to the equation

$$C_2H_4Br_2 + 2NH_3O = C_2H_4(NH_2O,HBr)_2.$$

To determine its constitution, the compound was reduced by boiling it with fuming hydriodic acid, and the base formed was liberated and distilled into aqueous hydrochloric acid; the hydrochloride thus obtained was converted into the platinochloride, and two separate fractions of the latter were ignited.

0·3872 gave 0·1706 Pt. Pt = 44·1.

0·0359 „ 0·0157 Pt. Pt = 43·7.

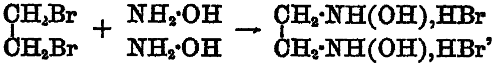
Ammonium platinochloride requires Pt = 43·9 per cent.

As ammonia was the only nitrogenous product of reduction, it follows that both the nitrogen atoms in the original base are linked to carbon by oxygen, and the constitution of the compound will be represented by the formula

$$\begin{array}{l} CH_2\cdot O\cdot NH_2\cdot HBr \\ | \\ CH_2\cdot O\cdot NH_2\cdot HBr \end{array}$$

(αα-ethylenedihydroxylamine or ethylenedioxylamine dihydrobromide).

If free hydroxylamine had the structure $H_2N\cdot OH$, it would seem more likely that it would react with ethylenic bromide according to the equation



$$\begin{array}{l}CH_2Br\\ |\\ CH_2Br\end{array} + \begin{array}{l}NH_2{\cdot}OH\\ NH_2{\cdot}OH\end{array} \rightarrow \begin{array}{l}CH_2{\cdot}NH(OH),HBr\\ |\\ CH_2{\cdot}NH(OH),HBr'\end{array}$$

yielding a β-hydroxylamine. The formation of this α-compound may therefore be regarded as additional evidence for regarding hydroxylamine in the free condition as possessing the structure $H_3N{:}O$, or at any rate acting tautomerically in the sense of that formula.

Ethylenic oxide, heated with a solution of hydroxylamine in methylic alcohol, also combines with it. The free base was not isolated, but by adding hydrochloric acid and evaporating, a hydrochloride was obtained, which appeared to behave in exactly the same manner as the hydrobromide obtained from ethylenic bromide. It was not, however, further examined.

Both the product from ethylenic oxide and that from ethylenic bromide, reduced Fehling's solution, even after purification. This may, however, have been due to a minute trace of hydroxylamine still present.

Ethylene, phosgene gas, and chloroform were each dissolved in a solution of hydroxylamine in methylic alcohol, and heated in a sealed tube at 100—120°, but no action occurred in any case.

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CVI.—*Alleged Isomerism of Potassium Nitrososulphate.*

By C. M. Luxmoore, D.Sc.

Raschig described (*Annalen*, 1887, **241**, 230) as "potassium nitrosulphite" a substance obtained by the action of nitric oxide on alkaline solution of potassium sulphite which gave with barium chloride a white precipitate of a barium salt soluble in hydrochloric acid, the clear solution soon becoming turbid through the gradual separation of barium sulphate. He mentioned in a footnote that on one occasion he obtained a nitrosulphite (= nitrososulphate) which gave scarcely any precipitate with barium chloride, but at once yielded a copious precipitate of barium sulphate on acidification. He suggested that the latter was an isomeride of the former which he evidently assumed to be identical with the nitrososulphate discovered by Davy and investigated by Pelouze (*Ann. Chim. Phys.*, 1835, [2], **60**, 151). That this assumption was correct appears to be taken for granted by Hantzsch, who has recently re-investigated the subject (*Ber.*, 1894, **27**, 3264). He was only able to obtain the latter of the two salts described by Raschig, but, as he found that its properties differed in some respects from those recorded by Pelouze, he concluded that the substance he obtained was isomeric with the Davy-Pelouze salt. Divers and Haga have also (this vol., 452) unsuccessfully endeavoured to obtain an isomeride of potassium nitrososulphate; and they maintain that no sufficient grounds exist for doubting the identity of the substance obtained by Hantzsch and themselves (Raschig's second salt) with the salt of Davy and Pelouze.

With a view to determining whether potassium nitrososulphate does exist in two isomeric forms, I have prepared it under various conditions, and have studied its properties in the light of those observations of Hantzsch which seem to show a difference between the salt he obtained and that described by Pelouze.

Most of my preparations have been obtained by the action of nitric oxide on potassium sulphite. The absorption has taken place (1) in a freezing mixture, (2) at the temperature of melting ice, (3) at the ordinary temperature, (4) commencing at about 40° C. The alkalinity of the potassium sulphite solution has also been very different in different cases, and the time of absorption of nitric oxide has varied from two or three hours to three days. In most cases, the bulk of the potassium nitrososulphate has been deposited in crystals during the absorption of nitric oxide. As the specimens thus obtained under most varied conditions appeared to be absolutely identical, careful search for any different products was made in the mother liquors, especially in two cases. Small further quantities of potassium nitrososulphate were thus obtained in an impure condition, but no substance behaving as Raschig's first salt did towards barium chloride could be detected.

I also prepared potassium nitrososulphate by the simultaneous absorption of nitric oxide and sulphur dioxide by potassium hydroxide solution (Pelouze, *loc. cit.*), thinking it possible that this method might yield an isomeride, if such existed. The product obtained was, however, identical with that yielded by the action of nitric oxide on potassium sulphite.

In the examination of the properties of potassium nitrososulphate (especially its behaviour on dry heating) described below, most of the experiments were repeated with specimens obtained under different conditions. As an additional evidence of identity, I prepared from several (inclusive of that obtained by the simultaneous absorption of nitric oxide and sulphur dioxide by potassium hydroxide) the silver salt, $KAgSN_2O_5$, described by Hantzsch (*loc. cit.*, p. 3272), which in each case behaved in the characteristic way that he describes; on touching it at one spot with a hot platinum wire, decomposition, accompanied by superficial brown coloration, proceeds throughout the whole mass, and the evolution of nitric oxide is evidenced by copious red fumes.

One of the principal points in which Hantzsch found a discrepancy between the properties of potassium nitrososulphate as obtained by him and as described by Pelouze, consisted in its behaviour on dry heating. Pelouze states that, subjected to a heat of 110° to 115°, it neither decomposes nor loses weight. At rather a higher temperature (about 130°), it is destroyed, evolving nitric oxide and leaving a residue of potassium sulphite. Hantzsch, on the contrary, found that it was slowly but completely decomposed at 95° into nitrous oxide and potassium sulphate, whilst if very suddenly heated from 20 to 26 per cent. was decomposed into nitric oxide and sulphite. Divers and Haga also found that it lost 10 per cent. of its weight at 95° in 2¼ hours when heated in dried hydrogen, and needed 12 hours heating at that temperature to complete the decomposition. They say: "Thus the loss of weight is slow and if a higher temperature (107°) mistaken for 110°, had been maintained for only a few minutes, it would have had so small an effect as probably to have deceived Pelouze." I find, however, that the loss of weight is much more rapid at first, as on gently heating (below 105°), the loss of weight in 15 minutes was 4 per cent., and in two other experiments in five and seven minutes the loss was 2½ and 3 per cent. respectively. It therefore seems impossible to explain how Pelouze could have arrived at the conclusion that the potassium salt does not lose weight at 110—115°. But the remainder of his statement quoted above exactly describes the phenomena as observed when one heats the substance in a test-tube in a sulphuric acid bath and notes the temperature by a thermometer with its bulb embedded in the salt; so long as the temperature of the substance lies below about 130°, no evidence of change is apparent, the decomposition into nitrous oxide proceeds imperceptibly, and the salt is perfectly quiescent. At a somewhat higher temperature a sudden, almost explosive, evolution of gas takes place, the temperature rises quickly, sometimes as high as 180°, and the test-tube becomes filled with red fumes from the nitric oxide evolved. As Divers has noticed, it is difficult to fix the explosive temperature; if the salt is heated up quickly, the thermometer has not time to acquire the true temperature, whilst if the heating is slow the explosive temperature is really that of a mixture containing much sulphate because of the considerable extent to which the nitrous oxide decomposition has proceeded before explosion. The temperatures I observed varied from 127° to 148° (Divers gives 91—108°, see below); probably the true temperature lies near 134°.

As Hantzsch and Divers and Haga have shown, the residue after explosion is a mixture of sulphate and sulphite. The residues I have obtained after explosion in a test-tube in the manner described have, in several cases, had the sulphite contained in them determined by titration of the dilute acidified solution with iodine. The results showed that from 14 to 22 per cent. of the nitrososulphate had decomposed into nitric oxide and potassium sulphite. By projecting the salt into a red-hot platinum crucible, I obtained in one case figures showing that 28 per cent. of the salt had decomposed in this way. It is evident that when Pelouze described the salt as decomposing into nitric oxide and sulphite, he based this on the manifest evolution of the former and the qualitative detection of the latter. He makes no mention whatever of any quantitative experiments on the subject.

When potassium nitrososulphate is heated in a test-tube as described above, its temperature is often observed to be considerably above that of the bath in which the test-tube is submerged; for instance, the temperature of the bath has been 117° when the salt has exploded at 130°.

Divers and Haga speak of the decomposition as an exothermic one, but they do not make it plain whether they refer to the gradual decomposition into nitrous oxide and sulphate, or only to the decomposition into nitric oxide and sulphite. They say, "When the salt does suddenly decompose, there is a marked rise of temperature, and this may have caused Pelouze to name 130° as the decomposition point." And they speak of the salt exploding at 91°, and again as reaching 108° before it exploded, but they do not state whether this refers to the temperature of the salt itself, or of the bath used as a source of heat. As a matter of fact, the gentle decomposition below 130° is accompanied by a considerable evolution of heat, which raises the temperature of the salt to the explosion point, and the further decomposition which then occurs is accompanied by a further rise of temperature. But whether this is due to the decomposition into nitric oxide is doubtful. If we reckon that in such an experiment one quarter of the salt has decomposed into nitrous oxide and sulphate before the explosion temperature is reached, we may take it that as only about one-quarter is converted into nitric oxide and sulphite, about one-half (more rather than less) undergoes the nitrous oxide decomposition at the moment of explosion; that is to say, of the nitrososulphate undecomposed at the moment of explosion, one-third only (rather less) yields nitric oxide and sulphite. This agrees with the fact that in the most sudden heating possible, the amount decomposed into nitric oxide and sulphite is always less than one-third.*

* The maxima recorded are Hantzsch, 26 per cent.; Divers and Haga, 29 per cent.; Luxmoore, 28 per cent.

It seems likely, therefore, that the heat or chemical energy supplied by the decomposition into nitrous oxide and sulphate is that which makes possible the other decomposition into nitric oxide and sulphite.

Another point of difference between Pelouze's and Hantzsch's observations lies in the stability of potassium nitrososulphate in aqueous solution. Pelouze, comparing it with the ammonium salt, says that one can even employ boiling water as a means of purification of this salt, it is only thus decomposed to a slight extent, and by washing *with very cold water* the crystals deposited, they can easily be freed from potassium sulphate. Hantzsch finds it to be readily decomposed in pure aqueous solution, even on gentle warming, but to be more stable in alkaline solution. This, however, as Divers and Haga observe, is entirely a matter of degree. Pelouze's salt was evidently not perfectly free from alkali and alkali carbonate, as is evident from its behaviour towards barium chloride (see below). Moreover, the sentence quoted above shows that he did observe some decomposition, as he not only speaks of freeing the crystals from potassium sulphate, but also mentions the need of using very cold water to avoid further decomposition. Repeating the experiment of Divers and Haga, I found that by adding to boiling water a drop or two of caustic potash, and then dissolving the nitrososulphate therein, and cooling down, about one-third could be recovered in a pure condition. The mother liquor contained some sulphate, but also unchanged nitrososulphate.

In regard to the behaviour of potassium nitrososulphate to barium chloride, Pelouze says (*loc. cit.*), "If, after adding a salt of baryta to the liquid, one collects the precipitate which is formed, washes it several times with aqueous potash. and then treats it with nitric acid, it dissolves completely, and one can thus be assured that no sulphate has been formed." As Divers and Haga have pointed out, the context shows that this precipitate is evidently due to impurities (probably carbonate, possibly sulphite). It cannot be such a barium salt as Raschig describes as obtained from his first salt, for Pelouze simply says it dissolves completely, and makes no mention of the clear solution afterwards depositing barium sulphate. Moreover, he lays stress on washing the precipitate, evidently to free it from barium nitrososulphate, which would else be instantly converted into sulphate on the addition of acid. Raschig's precipitate, on the other hand, is dissolved by acid without previous filtration. Pelouze, moreover, distinctly states that nitrososulphates are not precipitated by baryta water. None of the pure specimens of potassium nitrososulphate that I have prepared gave an immediate precipitate with barium chloride in the cold. Barium sulphate appears very quickly if the solution is not kept very cold, and almost instantaneously at 20°; on acidification, also, the precipitation of barium sulphate takes place immediately. Potassium nitrososulphate commences to decompose so readily that specimens only a day old frequently give a distinct opalescence with barium chloride.

In no case have I obtained any product from the action of nitric oxide on potassium sulphite showing the behaviour towards barium chloride that characterised Raschig's first salt. This behaviour is sufficient to show that it was not the Davy-Pelouze salt that Raschig obtained. Indeed he mentions no property by which it could be identified with the latter. In particular, the decomposition into nitric oxide and potassium sulphite (on which Hantzsch lays stress as distinguishing Pelouze's salt from his own preparation) is not mentioned by Raschig. It is impossible at present to say what Raschig's first salt was, but as he only determined the potassium and sulphur, and the figures obtained might have been yielded, as Divers and Haga have shown, by potassium dihydroxylamine sulphonate, there is no sufficient ground for believing it to have had the composition of potassium nitrososulphate, especially as no one has since succeeded in obtaining it from nitric oxide and potassium sulphite.

It has therefore been shown

(1.) That potassium nitrososulphate always has the same properties, under whatever conditions it is formed.

(2.) That Pelouze's account of the properties of this salt can be completely reconciled with the observations of Hantzsch, and of Divers and Haga, except the statement that it loses no weight at 110°, which is evidently a mistake.

(3.) That there is no evidence sufficient to warrant Raschig's first salt being regarded as isomeric with potassium nitrososulphate, still less as identical with the Davy-Pelouze salt.

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CVII.—*On the Freezing Points of Gold and Silver.*

By C. T. Heycock and F. H. Neville.

The recent paper by M. Le Chatelier, "On Certain Melting and Boiling Points" (*Compt. rend.*, 1895, **121**, 323), of which an abstract has been published by the Physical Society, calls attention to the discrepancies which exist between the various determinations of the melting points of gold and silver. We are obliged to differ from some of his conclusions with regard to these melting points, and propose in the present paper to give our reasons for doing so.

M. Le Chatelier speaks of "melting points" while we use the term "freezing point," but that this difference in nomenclature does not correspond to a real difference in temperature has been proved to us by the result of numerous experiments on the melting and freezing points of copper, gold, silver, and antimony, for when the metals are pure, the melting and freezing points are identical.

To take the case of gold first, we see that M. Le Chatelier, in a table of recently determined melting points of this metal, groups together the value 1037° given by Professor Callendar (*Phil. Mag.*, **33**, 222) and our determination 1061·7° (this vol., p. 189), from which it might be inferred that the discrepancy indicates the sort of error to which the method of platinum-resistance pyrometry is liable. He, however, takes no notice of the fact that Callendar's was a pioneer determination, undertaken in order to demonstrate the capabilities of his pyrometers, and that Callendar, in deducing from his experimental result the number 1037°, did not rigidly follow the method of calibration which was afterwards developed by Griffiths and himself and which we have always adhered to. That method requires that the resistance of the pyrometer should be determined at three standard temperatures, which must be accurately known on the air scale. In addition to ice and steam, we use the boiling point of sulphur (444·53°), while Callendar, in the work quoted by Le Chatelier, used for his third temperature the melting point of silver, assuming it, from Becquerel and Deville's experiments, to be 945°. Hence our results and Callendar's are not comparable; but Callendar's *pt** for gold, 902·3°, is only three or four degrees lower than ours, and the same is true for the *pt* 830°, which he finds for silver. In fact, if we use 960·7° C., the number obtained by us for the melting point of silver, instead of 945° C., and combine it according to Callendar's method with his platinum temperature of 902·3°, we obtain from his experiments the number 1060·8° C. as the melting point of gold. This is in very good agreement with our value 1061·7° C. We infer from this that there is no inconsistency between Callendar's results and our own, and that if Callendar had standardised his thermometer on the boiling point of sulphur, his Centigrade temperatures for the melting points of gold and silver would have been extremely near our own. We do not advance the above as an argument that our numbers are necessarily correct, but that the method does not give results which are inconsistent among themselves. We are, of course, aware that the melting points of gold, silver, and copper which we have found, are arrived at by a somewhat extreme use of an extrapolation formula, and we look forward with much interest to the direct determination of these constants by means of an air thermometer. Meanwhile the fair agreement of our numbers with those of Holborn and Wien, and the fact that M. Le Chatelier himself is now willing to adopt 1060° for the melting point of gold, afford considerable evidence that the extrapolation formula proposed by Callendar will bear the strain we have put upon it. This has been a surprise to ourselves, for we should have expected the formula to give numbers which were lower than the standard ones, and we still think it possible that the true melting points on the air scale will turn out to be somewhat higher than the numbers we have given.

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* For "*pt*," that is platinum temperature, see this vol., p. 161.

Passing now to the melting point of silver, we cannot at present agree with M. Le Chatelier as to the action of gases on the molten metal. In the *Zeit. physikal. Chem.*, 1891, 8, 186, he states that the melting point of silver can be lowered as much as 30° through the absorption of hydrogen, and in the *Compt. rend.* (*loc. cit.*) he says that this melting point should be determined in an oxidising atmosphere "on account of the important modification experienced by the melting point in a reducing atmosphere." Since these conclusions are opposed to the previous work of Callendar and to our own results obtained in 1894, we have felt it necessary to make some further experiments, and we wish to lay the results before the Society.

The silver was melted in a small Fletcher blast furnace, and the temperature of freezing was determined by means of a platinum-resistance pyrometer of the Callendar-Griffiths type. Two thermometers were used, one for the series of experiments given in Table I, the other for the series of Table II. They were calibrated according to the method described by us (this vol., p. 160). The crucibles, 10 cm. deep and 3 cm. wide, were so arranged that no furnace gases could reach the metal except by diffusion through the walls of the crucible. When we wished to expose the metal to the action of a gas, a current of this gas was led into the crucible through a clay-pipe stem which sometimes ended immediately above the surface of the metal, and was at other times plunged to the bottom of the crucible, so that the gas bubbled through the molten metal. The mouth of the crucible was closed by asbestos screens in order to prevent too rapid loss of heat by radiation, and to minimise the diffusion of air.

In the series of experiments given in Table I, the silver, weighing 290 grams, was contained in a salamander (plumbago and clay) crucible. In this series, the weight of silver was perhaps too small, and therefore the immersion of the pyrometer was insufficient to give standard numbers with so rapid a rate of cooling; but experiments 5 to 11, in which hydrogen was used, only differ by 1·6 from

960·7, which for the present we regard as our standard number. In the tables, we give the time at which the freezing took place, and this column shows how long the different gases were allowed to act, for when a change in the atmosphere was made, it was generally immediately after a reading.

TABLE I.—*Freezing Point of Silver in Plumbago Crucible.*

Nature of gas used.	Experiment No.	Moment of freezing.	Temperature of freezing in degrees centigrade.	Change in freezing point.
Coal gas on surface. No spitting	1	p.m. 4.0	958·71	—
Air. Spitting observed	2	4.15	957·84	−0·87
„ Violent spitting................	3	4.30	956·10	−2·61
Hydrogen. Slow current over surface..	4	4.35	956·36	−2·35
„ Strong „ „ ..	5	4.45	959·11	+0·40
„ „ „ „ ..	6	4.50	959·11	+0·40
„ Forced through the metal .	7	5.0	959·11	+0·40
„ „ „ „ ..	8	5.7	959·11	+0·40
„ Forced through the metal and carbon stirrer	9	5.15	959·14	+0·43
Hydrogen. Forced through the metal and carbon stirrer.................	10	5.22	959·14	+0·43
Hydrogen replaced by carbon dioxide..	11	5.30	959·13	+0·42
„ „ „ „ ..	12	5.45	(958·85*	+0·14)

In the above series, the plumbago walls of the crucible prevented diffusion of oxygen, and also minimised the action of the air on the surface of the metal in experiments 2 and 3.

Experiments 4 to 10 show that whether the hydrogen is absorbed by the silver, as M. Le Chatelier thinks, or merely sweeps out the oxygen, as we are disposed to believe, it in either case *raises and does not lower* the freezing point. The fact that experiments 7 and 8, in which the hydrogen was bubbled through the molten silver, give the same freezing point as experiment 6, shows that absorption, if it exists, is slight, and the result of experiment 11, in which carbon dioxide was passed into the crucible instead of hydrogen, is to our minds conclusive against the view that hydrogen has any other effect than that of protecting the metal against oxygen. It may be said that even in experiment 1 the silver was saturated with hydrogen, but if so, the first action of the air in experiment 2 should have been to *raise* the freezing point, unless we assume that oxygen and hydrogen can exist together in solution in molten silver.

The series of Table II differs from the previous one, in the larger

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* This was not the freezing point observed, but a lower, very steady, temperature.

get in air or an ordinary oxidising atmosphere. This value is Violle's value, 5° or 6° below our standard of 960·7°. Experiments 3 to 8 show the value we are likely to get under the most favourable conditions for the absorption of oxygen; we believe the freezing point of silver saturated with oxygen will prove to be near 940°.

Experiments 9 to 15 show the current of nitrogen sweeping out the oxygen and gradually raising the freezing point; but it does not look as if the action of the nitrogen, even if prolonged, would have raised the freezing point up to the hydrogen value. This may be due to the nitrogen being unable to expel all the oxygen, to the continual entry of oxygen through the walls of the crucible, or to the nitrogen being itself somewhat soluble, and so producing a specific lowering of the freezing point. Experiments 16 to 18 show how perfectly hydrogen, even without the presence of carbon, brings the freezing point up to its standard maximum value of about 960·5°. This is almost exactly the mean of the results we obtained using coal gas and a carbon crucible (this vol., p. 188).

These results appear to us to prove that the freezing point of silver is highest and most constant in a reducing atmosphere, and that hydrogen, coal gas, or carbon together with carbon dioxide, are equally effective. This fact, without explanation, is sufficient to establish the value of the freezing point of silver as a standard temperature.

We think the above-mentioned experiments offer many grounds for the view that these reducing agents act simply as removers of oxygen, and have no effect of their own on the silver, but the most conclusive proof of this lies in the behaviour of pure silver when freezing or melting in a reducing atmosphere. Under this condition there is no trace of spitting, and from the moment when solid begins to form to the moment of complete solidification the temperature is constant instead of slowly falling, as would be the case were there anything in solution. Moreover, the melting point is the same as the freezing point. These are characteristics of a pure substance; they are not noticed when the silver is in an oxidising atmosphere, but they are noticed when it is in a reducing atmosphere.

We do not see how to reconcile our results with those of M. Le Chatelier, but it has occurred to us that possibly the wires of his thermo-couple may be affected by reducing gases such as carbon monoxide and hydrogen. The paper in the *Comptes rendus* does not contain the details of M. Le Chatelier's experiments, and therefore we cannot say whether this contingency is excluded by the arrangement of his apparatus.

It would not be very difficult to determine the freezing point in a vacuum, and thus settle the question.

CVIII.—*The Action of certain Acidic Oxides on Salts of Hydroxy Acids.* Part II.

By George G. Henderson, D.Sc., M.A., and David Prentice.

In a former communication to the Society (this vol., 102), it was shown by one of us that arsenious oxide reacts with primary alkali tartrates to form compounds of the same type as tartar emetic, and that those may be regarded as derivatives of tartrarsenious acid, $HO\cdot As(C_4H_5O_6)_2$. It was also stated that both antimonious and arsenious oxides appeared to form compounds with other hydroxy-acids, but not with acids which contain no alcoholic hydroxyl group. The present paper gives the results obtained by acting with those oxides on salts of citric, malic, lactic, and mucic acids, these having been selected as readily accessible acids containing different numbers of hydroxyl and carboxyl groups.

Antimonious Oxide and Primary Citrates.

Antimonious oxide, when added in small quantities at a time to a boiling aqueous solution of primary potassium citrate, dissolved fairly readily until the saturation point was reached; it was found that about 6 mols. of the citrate dissolved 1 mol. of the oxide. Excess of oxide was added, and after the boiling had been continued for some time, the solution was filtered, concentrated on the water bath, cooled, and mixed with about three times its volume of alcohol; the white, amorphous precipitate thus produced became crystalline after standing for some hours in contact with the liquid, and the crystals, after being washed with alcohol and dried in the air, were found to contain 18 per cent. of antimony. The salt was then recrystallised from hot dilute alcohol and analysed.

	Found.	Calculated for $SbOK_3(C_6H_6O_7)_2,2H_2O$.	Calculated for $SbK_3(C_6H_5O_7)_2,2H_2O$.
K	17·83	17·46	17·97
Sb	18·38	17·93	18·43
H_2O ...	5·28	5·38	5·52

The antimony in this and also in the other salts described below, was estimated by titration with standard iodine solution; the water of crystallisation in this salt was determined by heating at 125°, as apparently the whole was not expelled at lower temperatures.

The *potassium salt* thus obtained crystallises in small, colourless needles, readily soluble in cold water and fairly soluble in dilute alcohol. From a cold concentrated aqueous solution, it separates as a colourless syrup, which crystallises after a long time; from a hot solution, it usually separates in the crystalline state. Apparently it is not decomposed by heat below 140—145°, but at this temperature it begins to turn brown, and at 160° it blackens. An aqueous solution of the salt is strongly acid to litmus, but the addition of caustic alkalis causes immediate decomposition and precipitation of antimonious oxide; mineral acids have a similar effect. Experiment showed that 3 mols. KOH were required to neutralise 1 mol. of the salt, and that the whole of the antimony was then precipitated.

Several attempts were made to prepare salts containing proportions of potassium different from the above, but in each case without success. Thus, for example, secondary potassium citrate gave the same compound as the primary salt.

Thaulow (*Annalen*, 1838, **27**, 334) describes the preparation of a "double citrate of antimony and potash," to which he gave the formula (using modern notation) $SbC_6H_5O_7,K_3C_6H_5O_7,2\frac{1}{2}H_2O$. The compound which we obtained is undoubtedly identical with this salt.

The corresponding *sodium salt* was prepared in the same way as the potassium salt, and was purified by recrystallisation from hot dilute alcohol, from which it separates as a powder consisting of minute needles.

	Found.	Calculated for $SbONa_3(C_6H_6O_7)_2,H_2O$.	Calculated for $SbNa_3(C_6H_5O_7)_2,H_2O$.
Sb....	19·97	19·90	20·51
H_2O...	3·58	2·98	3·07

The water was determined at 105°.

The *ammonium salt* was prepared similarly. It crystallises better than the others, separating from hot dilute alcohol in shining, colourless prisms.

	Found.	Calculated for $SbO(NH_4)_3(C_6H_6O_7)_2,H_2O$.	Calculated for $Sb(NH_4)_3(C_6H_5O_7)_2,H_2O$.
Sb....	20·20	20·40	21·05
H_2O...	3·03	3·06	3·15

The water was determined by exposure in a vacuum over sulphuric acid.

Both the sodium and ammonium salts closely resemble the potassium salt as regards solubility, reaction of solution, and behaviour towards alkalis and acids, but the ammonium salt is less stable than the others. When heated, it begins to decompose at 105°, and is completely charred at 120°.

The *barium salt* was obtained by precipitation. When aqueous solutions of barium chloride and of the potassium salt are mixed, no visible action occurs, even when highly concentrated solutions are employed; but if the mixture is left for several hours, or is heated on a water bath for a short time, a white precipitate slowly separates;

it usually appears amorphous, but is crystalline when very slowly formed. To purify the salt, it is dissolved in water, from which it separates as a white powder when the solution is left to evaporate spontaneously. It is only very sparingly soluble in cold, but fairly soluble in hot water. If an aqueous solution is concentrated too far on the water bath, the salt decomposes and antimonious oxide is precipitated.

Analysis of the salt showed, as might be expected from the way in which it is formed, that its composition is not identical with that of the potassium salt.

	Found.	Calculated for $SbOBa_3(C_6H_6O_7)_3,10H_2O$.	Calculated for $SbBa_3(C_6H_5O_7)_3,10H_2O$.
Ba....	31·03	31·71	32·15
Sb....	9·29	9·25	9·39
H_2O...	13·84	13·88	14·08

What appears to be another barium compound is obtained under different conditions. If the calculated quantity of barium acetate is added to a solution of the potassium salt, the barium compound just described is formed in the same way as when barium chloride is used, but if barium acetate is added in considerable excess a white precipitate comes down at once; this contains only 6·5 per cent. of antimony, and is fairly soluble in cold water. When a cold solution of it is heated to about 60°, a white precipitate separates which redissolves when the solution is heated to boiling; possibly this substance is a double salt, but we did not succeed in getting it satisfactorily purified, for it decomposes, if its solution is concentrated or even when left to evaporate spontaneously.

The addition of silver nitrate to an aqueous solution of the potassium salt produces a white, flocculent precipitate which, when dry, forms a white powder; it is probably a mixture, for it contains 44·25 per cent. of silver and 5·7 per cent. of antimony, a composition which does not agree with any simple formula corresponding to those of the other salts. It is quite insoluble in water, but dissolves in hot nitric acid, and when hydrochloric acid is added to the solution a white precipitate is formed which dissolves completely in excess of hydrochloric acid. If it is suspended in water and a 10 per cent. solution of ammonia added drop by drop with constant agitation, it dissolves completely, and the solution, when warmed, gives a deposit of metallic silver. If the silver compound is treated directly with excess of 10 per cent. ammonia, it is almost at once decomposed, silver separating out.

A compound, which may be regarded as the *free acid* corresponding with the salts described above, was prepared from the barium salt; this was suspended in water, and rather less than the calculated quantity of dilute sulphuric acid added very gradually with continuous stirring, the liquid filtered, concentrated on the water bath, and finally left to evaporate spontaneously As evaporation proceeded, a colourless syrup gradually separated, which, when left exposed to the air for several days, solidified for the most part in fern-like crystals; these, after being washed with a little cold water and pressed between folds of filter paper, were found to contain 22·22 per cent. of antimony. The substance, purified by dissolving it in water and allowing the solution to evaporate spontaneously as before, was then found to contain 24 51 per cent. of antimony, but, owing to its instability, it was difficult to obtain any quantity of it in a pure state. The percentage of antimony found agrees fairly well, however, with that calculated from the formula $HO{\cdot}Sb(C_6H_7O_7)_2$ (Sb = 23 12 per cent.).

The acid crystallises in groups of small, colourless plates, which gradually become white and opaque owing to decomposition into antimonious oxide and citric acid. It dissolves very easily in cold water, and the solution has a strongly acid reaction, and decomposes carbonates of the alkalis; when neutralised with the calculated quantity of potassium carbonate, it gives the potassium salt already described. The addition of a drop or two of a mineral acid to its solution causes immediate decomposition.

Citric acid in aqueous solution dissolves about one-seventh of its weight of antimonious oxide on prolonged boiling with it, and the solution when left to evaporate deposits a syrup which gradually becomes crystalline when left exposed to the air. The crystals, which are easily soluble in water, contain antimony, but have not yet been further investigated.

Arsenious Oxide and Primary Citrates.

With primary citrates of the alkalis, arsenious oxide forms compounds which are similar to the corresponding antimony salts, though less stable than the latter.

The *potassium salt* was obtained by dissolving arsenious oxide, in small quantities at a time, in a boiling solution of primary potassium citrate, allowing the solution to cool, and then adding about three volumes of alcohol. A thick, colourless syrup was precipitated, which became crystalline on standing for several hours in contact with the liquid; this precipitate was collected, washed with a little dilute alcohol, and analysed after recrystallisation from hot dilute alcohol.

	Found.	Calculated for $AsOK_3(C_6H_6O_7)_2,4\frac{1}{2}H_2O$.	Calculated for $AsK_3(C_6H_5O_7)_2,4\frac{1}{2}H_2O$.
K	17·86	17·48	17·97
As	11·44	11·21	11·52
H_2O ...	12·48	12·10	12·44

The salt forms beautiful prismatic crystals which are easily soluble in cold water and fairly so in dilute alcohol; an aqueous solution is strongly acid to litmus. With alkalis and mineral acids, it behaves like the corresponding antimony salt, and generally resembles the latter, but is less stable, for if its aqueous solution is concentrated by evaporation on the water bath the salt gradually decomposes and arsenious oxide crystallises out. If an aqueous solution is left to evaporate spontaneously, the salt separates as a colourless syrup, which only crystallises after a long time.

In this case also, an attempt was made to prepare a salt containing a different proportion of potassium by using the secondary instead of the primary citrate, but the product was identical with that just described. Other experiments were made by adding 1 and 2 mols. respectively of potassium carbonate to 1 mol. of the salt, and also by neutralising it completely with potassium carbonate, but apparently in every case decomposition ensued. It was found that 3 mols. of caustic potash were required to neutralise 1 mol. of the salt, which was simultaneously decomposed into a mixture of arsenious oxide and potassium citrate.

The *sodium* and *ammonium salts* were prepared in the same way as the potassium salt, which they resemble in properties. Both separate in the form of a syrup on adding alcohol to their aqueous solutions, and the syrup becomes crystalline on standing, though more slowly than in the case of the potassium salt.

The sodium salt crystallises from dilute alcohol in colourless plates, easily soluble in cold water.

	Found.	Calculated for $AsONa_3(C_6H_6O_7)_2,3\frac{1}{2}H_2O$.	Calculated for $AsNa_3(C_6H_5O_7)_2,3\frac{1}{2}H_2O$.
As....	11·96	12·43	12·82
H_2O...	10·01	10·44	10·77

The ammonium salt crystallises from dilute alcohol in tufts of small, shining needles. As it is extremely deliquescent, the crystals were collected, washed with alcohol, allowed to stand over sulphuric acid for some hours, and then put into stoppered tubes. The salt dried in this way gave the following figures on analysis.

	Found.	Calculated for $AsO(NH_4)_3(C_6H_6O_7)_2,H_2O$.	Calculated for $As(NH_4)_3(C_6H_5O_7)_2,H_2O$.
As....	13·78	13·81	14·29
H_2O...	2·43	3·31	3·43

The water was determined by exposure in a vacuum over sulphuric acid and the result is naturally low owing to the manner in which the salt was dried.

A definite barium salt is not formed by precipitation, as is the case with the antimony compounds; barium chloride indeed gives a white amorphous precipitate at once when added to a solution of the potassium salt, but this, after being allowed to stand for some time and then washed with cold water and dried, contained only 1·4 per cent. of arsenic, so that if the precipitate was a barium salt it was very unstable.

Antimonious Oxide and Primary Malates.

The only compound as yet obtained by the interaction of antimonious oxide and primary malates is the *potassium salt;* the preparation of this was troublesome, for it was found that when the substances were heated together in presence of water, some of the malate always remained unaltered, and was precipitated by alcohol along with the new salt. The following method gave the best results:—Antimonious oxide was added in small instalments to a boiling dilute solution of primary potassium malate until some remained undissolved; after the boiling had been continued for some hours the solution was filtered, concentrated on the water bath, cooled, and left in a vacuum over sulphuric acid. The first crop of crystals, as a rule, contained varying proportions of antimony, and appeared to be a mixture of unaltered malate and the new salt; it was set aside and used for preparing fresh quantities of the substance. The second crop of crystals consisted principally of the new salt, but required three or four recrystallisations from water, in the manner described, before the composition became constant. The crystals were then washed with a little dilute alcohol, pressed between folds of filter paper, and dried in air. Analysis of the air-dried salt showed that its composition was complex, but the figures obtained agree fairly well with those calculated for the formula given.

	Found.	Calculated for $(SbO)_3K_4(C_4H_5O_5)_6,3H_2O$.
K..........	11·42	11·02
Sb..........	25·59	25·44
H_2O........	4·32	3·81

The water was determined by drying in a vacuum. The salt crystallises in beautiful, short, colourless prisms which are very soluble in cold water, and readily in dilute alcohol. It may be recrystallised from hot water, but if a solution is boiled for a short time the salt decomposes, and antimonious oxide is deposited. It turns brown and loses weight rapidly when heated to 130°. The addition of potassium hydroxide or of hydrochloric acid to a solution of the salt at once decomposes it.

Pasteur (*Ann. Chim. Phys.*, 1851, [3], **31**, 85) obtained a crystalline "malate double d'ammoniaque et d'antimoine" by dissolving antimonious oxide in a hot solution of primary ammonium malate Neither the composition nor the formula of this salt is given, so that, possibly, it was similar in composition to the potassium salt prepared by us.

When the calculated quantity of barium acetate is added to a solution of the potassium salt, no precipitate is formed, but if sufficient alcohol to produce a turbidity is added, a white powder is gradually deposited; this, which is soluble in water and contains antimony, is probably the corresponding barium salt, but has not yet been further examined. If excess of barium acetate is mixed with a solution of the potassium salt, a white, gelatinous precipitate is at once thrown down; dried by exposure to the air, it assumes the form of a white powder which does not wholly dissolve in boiling water, but is freely soluble in hydrochloric acid. It contains about 40 per cent. of antimony, and is possibly a mixture of antimonious oxide and barium malate.

Arsenious Oxide and Potassium Malate.

Arsenious oxide dissolves readily in a boiling aqueous solution of primary potassium malate; but if a compound corresponding with the antimony salt is formed, it is so unstable that we have not yet succeeded in isolating it. If alcohol is added to the solution, a crystalline precipitate is thrown down, but it contains only a trace of arsenic, and, if the solution is concentrated on the water bath or left to evaporate spontaneously, arsenious oxide gradually crystallises out, leaving slightly impure potassium malate behind. In one experiment, malic acid, potassium carbonate, and arsenious oxide were boiled with water until the oxide had dissolved completely, and then alcohol was added; a colourless syrup containing arsenic was precipitated, but it has not yet been possible to get this in a crystalline condition.

Antimonious and Arsenious Oxides and Lactates.

Both antimonious and arsenious oxides dissolved in boiling solutions of alkali lactates, and when the solutions were allowed to evaporate spontaneously or were mixed with alcohol, colourless syrups were obtained which did not solidify even when left in a vacuum over sulphuric acid for many weeks. Dried at 105°, they form colourless, vitreous masses. They are extremely deliquescent, and very soluble in water. When dried in a vacuum over sulphuric acid, they were found to contain 5·1 per cent. of antimony and 4·3 per cent. of arsenic respectively; the arsenic compound when dried at 105° contained 7·4 per cent. of arsenic. It is possible that these substances are mixtures of unaltered lactate with derivatives of lactic acid and the oxides similar to those formed by other acids, but we did not succeed in separating them into their constituents either by fractional precipitation or fractional solution in dilute alcohol. The following experiment seems to justify the supposition that reaction does take place; arsenious oxide (1 mol.) was dissolved in a hot solution of barium lactate (2 mols.), the solution boiled for some hours, and then left to evaporate spontaneously; a colourless syrup separated which, when tested qualitatively, was found to contain a large proportion of arsenic as well as barium. As it showed no signs of crystallising over sulphuric acid, it was left exposed to the air, and at the end of two weeks the clear, thick syrup changed spontaneously to a white, amorphous mass. When this solid mass was treated with cold water barium lactate went into solution and a residue of arsenious oxide was left. Perhaps, therefore, the syrupy substance was a compound formed by interaction of arsenious oxide and barium lactate, which decomposed on being left for some time exposed to the air.

Antimonious Oxide and Primary Mucates.

The *potassium salt* is the only one as yet prepared, and considerable difficulty was experienced in obtaining it in a state of purity, for although antimonious oxide dissolves slowly in a boiling solution of primary potassium mucate, the new salt is not readily formed, and is easily decomposed by boiling with water. The best method is to add the oxide in small quantities at a time to a dilute aqueous solution of the mucate heated to boiling; the oxide dissolves slowly until there is about 1 mol. in solution for each 8 mols. of mucate present, excess of oxide is then added, and the boiling continued for several days. The filtered solution, concentrated on the water bath as far as possible without decomposing the salt, and allowed to cool gradually, deposits a white powder. This, after being washed with cold water and dried in the air, was analysed.

	Found.	Calculated for $2SbOKC_6H_8O_8,KC_6H_9O_8,6H_2O$.
K..........	10·50	10·42
Sb..........	20·99	21·39
H_2O........	9·99	9·62

The water was determined at 95—100°.

The new compound, which, according to the analysis, must be regarded as a double salt, is obtained in the form of a white, finely crystalline powder, which is only sparingly soluble in cold, but fairly in hot water. It is decomposed when boiled with water, unless excess of antimonious oxide be present, and also if an aqueous solution is concentrated too far on the water bath. It is also easily decomposed by heat, turning brown if exposed for some time to a temperature of

100—105°. It is precipitated from its aqueous solution by the addition of alcohol.

When this salt was recrystallised repeatedly, another salt was obtained, which resembled it closely in appearance and properties, but differed in containing 26 per cent. of antimony. A salt of the composition $SbOKC_6H_8O_8,4H_2O$ would contain 26·37 per cent. of antimony, so it may be concluded that the double salt described above is split up by repeated recrystallisation from water, and yields the simple salt.

Arsenious Oxide and Primary Mucates.

Arsenious oxide was also found to dissolve in a boiling solution of primary potassium mucate; a slight excess of the oxide was used, and, after boiling for several hours, the solution was concentrated, cooled, filtered from any arsenious oxide which separated, and mixed with alcohol. An amorphous precipitate was obtained, which, on standing in contact with the liquid, formed small, needle-shaped crystals. Two analyses of different preparations gave 16·13 and 18·07 per cent. of arsenic respectively, while a substance of the formula $AsOKC_6H_7O_8,3H_2O$ would contain 18·20 per cent. of arsenic. This *potassium salt* is not stable, and decomposes when an aqueous solution is left to evaporate spontaneously.

As regards the constitution of the compounds described above, it will be observed that the salts formed by the interaction of antimonious and arsenious oxides with the citrates might be represented as double citrates of antimony or arsenic and potassium, barium, &c., $SbC_6H_5O_7,K_3C_6H_5O_7,2H_2O$; $SbC_6H_5O_7,Ba_3(C_6H_5O_7)_2,10H_2O$; $AsC_6H_5O_7,(NH_4)_3C_6H_5O_7,H_2O$, &c. On the other hand, in the case of almost all of the compounds described, the analytical figures agree better with the formulæ calculated on the supposition that the salts contain the radicles $(SbO)'$ and $(AsO)'$; thus, the formulæ would be, for the citric acid compounds, $(SbO)KC_6H_6O_7,K_2C_6H_6O_7,2H_2O$; $(SbO)BaC_6H_5O_7,2BaC_6H_6O_7,10H_2O$; $(SbO)C_6H_7O_7,C_6H_8O_7$;

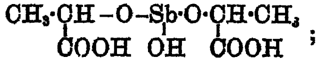
$$(AsO)(NH_4)C_6H_6O_7,(NH_4)_2C_6H_6O_7,H_2O, \text{ \&c.};$$

for the malic acid compound, $3(SbO)C_4H_5O_5,2K_2C_4H_4O_5,C_4H_6O_5,3H_2O$ or $3(SbO)KC_4H_4O_5,KC_4H_5O_5,2C_4H_6O_5,3H_2O$; for the mucic acid compounds, $2(SbO)KC_6H_8O_8,KC_6H_9O_8,6H_2O$ and $(SbO)KC_6H_8O_8,4H_2O$.

But it must be noted that, as stated in our former paper (*loc. cit.*), apparently it is only hydroxy-acids which react with antimonious or arsenious oxide to form compounds such as those described, that is, the presence of one or more alcoholic hydroxyl groups in the acid is essential to the reaction, hence those groups play an important part in it. It is difficult to account for this if it is held that the $(SbO)'$

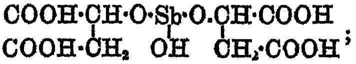
or (AsO)′ is present in those compounds as a basic radicle, displacing the hydrogen of a carboxyl group, but a not unreasonable explanation is found if it is assumed that the SbO or AsO radicle displaces the hydrogen of an alcoholic hydroxyl group, giving rise to compounds which may be compared with the alkyl derivatives of hydroxy-acids. Another explanation is, however, possible, and indeed seems preferable, in the case of at least some of the new salts. In the compounds of citric acid, which contain one alcoholic hydroxyl group, there is 1 atom of antimony or arsenic for 2 mols. of the acid (regarding the barium compound as a double salt); in the compound of malic acid, which also contains one hydroxyl group, although the composition of the salt is more complex, the same ratio of 2 mols. of acid to 1 atom of antimony appears; tartaric acid, which contains two alcoholic hydroxyl groups, forms compounds with both antimonious and arsenious oxides in which there is 1 atom of antimony or arsenic for 1 mol. of the acid; mucic acid contains four alcoholic hydroxyl groups, and forms a compound in which, if we regard it as a double salt, there is again 1 atom of antimony for 1 mol. of acid. It seems then, not only that the formation of such compounds depends on the presence of alcoholic hydroxyl groups in the acid, but also that the composition of the compound depends on the number of those groups in the molecule of the acid. This is explicable on the assumption that the compounds are salts of substituted antimonious or arsenious acids, in which the radicle of the organic acid is linked on to the antimony or arsenic by the oxygen of one or more hydroxyl groups. The formulæ of such acids might be represented as follows.

Antimonio-lactic acid,



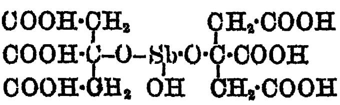
$$\begin{array}{ccccccc} \mathrm{CH_3\cdot} & \mathrm{CH} & \mathrm{-O-} & \mathrm{Sb} & \mathrm{\cdot O\cdot} & \mathrm{CH} & \mathrm{\cdot CH_3} \\ & | & & | & & | & \\ & \mathrm{COOH} & & \mathrm{OH} & & \mathrm{COOH} & \end{array};$$

Antimonio-malic acid,



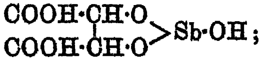
$$\begin{array}{ccccccc} \mathrm{COOH\cdot} & \mathrm{CH} & \mathrm{\cdot O\cdot} & \mathrm{Sb} & \mathrm{\cdot O.} & \mathrm{CH} & \mathrm{\cdot COOH} \\ & | & & | & & | & \\ \mathrm{COOH\cdot} & \mathrm{CH_2} & & \mathrm{OH} & & \mathrm{CH_2} & \mathrm{\cdot COOH} \end{array};$$

Antimonio-citric acid,



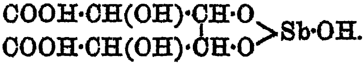
$$\begin{array}{ccccccc} \mathrm{COOH\cdot} & \mathrm{CH_2} & & & & \mathrm{CH_2} & \mathrm{\cdot COOH} \\ & | & & & & | & \\ \mathrm{COOH\cdot} & \mathrm{C} & \mathrm{-O-} & \mathrm{Sb} & \mathrm{\cdot O\cdot} & \mathrm{C} & \mathrm{\cdot COOH} \\ & | & & | & & | & \\ \mathrm{COOH\cdot} & \mathrm{CH_2} & & \mathrm{OH} & & \mathrm{CH_2} & \mathrm{\cdot COOH} \end{array};$$

Antimonio-tartaric acid,



$$\left.\begin{array}{l} \mathrm{COOH\cdot CH\cdot O} \\ \qquad\ \ | \\ \mathrm{COOH\cdot CH\cdot O} \end{array}\right> \mathrm{Sb\cdot OH};$$

Antimonio-mucic acid,



$$\left.\begin{array}{l} \mathrm{COOH\cdot CH(OH)\cdot CH\cdot O} \\ \qquad\qquad\qquad\quad | \\ \mathrm{COOH\cdot CH(OH)\cdot CH\cdot O} \end{array}\right> \mathrm{Sb\cdot OH}.$$

The formulæ for the derivatives of arsenious acid would be strictly analogous.

Compounds of this nature appear to be capable of existence, for an unstable antimonio-tartaric (tartrantimonious) acid has been isolated by Clarke and Stallo (*Amer. Chem. J.*, 1880, **2**, 319), and it has been shown by one of us (this vol., 102) that in all probability a corresponding arseniotartaric (tartrarsenious) acid can be obtained in solution, whilst a substance, which appears to be antimonio-citric acid, is described in the present paper. It is hardly necessary to point out, in addition, that the borotartrates, of which a number have been prepared, may be regarded as salts of a boro-tartaric acid, $C_4H_4O_6{:}B{\cdot}OH$.

It cannot be said that the results we have obtained so far permit of a decision as to the constitution of the salts mentioned, but it is hoped that some light may be thrown on the question by experiments which are in progress on the behaviour of other acidic oxides with hydroxy-acids of the aliphatic series, and of antimonious and arsenious oxides with hydroxy-acids of the aromatic series.

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CIX.—*Acidylthiocarbimides.*

By Augustus E. Dixon, M.D.

A few months ago (this vol., 565), it was shown by the author, in conjunction with R. E. Doran, that lead thiocyanate, interacting, in presence of anhydrous benzene, with the chlorides of succinic and phthalic acids respectively, affords, instead of the corresponding thiocyanates, acidic compounds of the thiocarbimide class. With succinyl chloride, for example, the reaction takes place almost quantitatively as follows.

$$C_2H_4(COCl)_2 + Pb(SCN)_2 = PbCl_2 + C_2H_4(CO{\cdot}NCS)_2.$$

Owing to the instability of the latter product, all attempts to isolate it in a pure condition proved unsuccessful; but by bringing the substance, in solution, into contact with ammonia, with primary or secondary amines, with phenylhydrazine, or with alcohol, the corresponding thioureas, semithiocarbazide, or thiourethane were formed, thus establishing beyond question its thiocarbimidic character.

In the present communication, an account is given of the preparation, in solution, of the valeryl and cinnamoyl compounds, together with a number of their derivatives, and the process has been further extended by Mr. Doran to the chlorocarbonic "esters," with results which he hopes shortly to lay before the Society.

Part I.—*Derivatives of Valerylthiocarbimide.*

Valeryl chloride, diluted with about three times its own volume of anhydrous benzene, was heated with a little more than the calculated amount of pure, well-dried lead thiocyanate to the boiling point of the mixture, using a reflux condenser. The solution gradually changed colour, becoming fine, clear, golden yellow, and in about a quarter of an hour was free from chlorine; it was filtered from lead chloride and unaltered thiocyanate by means of the pump, and, for convenience in use, was diluted with more benzene, so that (assuming the yield to be quantitative) each litre should contain a gram-molecule of dissolved product. The solution had a barely perceptible odour of valeric acid, otherwise it possessed little smell except of benzene, but its vapour attacked the eyes strongly, exciting, like acetylthiocarbimide, a copious flow of tears.

When shaken up with cold water, or exposed to moist air, the dissolved thiocarbimide gradually decomposed, yielding thiocyanic and valeric acids—

$$C_4H_9{\cdot}CO{\cdot}NCS + H_2O = C_4H_9{\cdot}COOH + HSCN;$$

on the other hand, the mixture with alcohol was readily desulphurised by boiling with alkaline lead tartrate, or in the cold by the addition of ammoniacal silver nitrate. In the experiments to be described, the above-mentioned benzene solution was employed.

ab-*Valerylphenylthiocarbamide*, $C_4H_9{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_6H_5$.*

Molecular proportions of valerylthiocarbimide and alcoholic solution of aniline were mixed; some evolution of heat occurred, and after concentrating and allowing to cool, large, vitreous, flattened prisms separated, which, when further purified by recrystallisation from alcohol, melted at 98—99° (corr.). The yield amounted to about 67 per cent. of that theoretically obtainable according to the equation—

$$C_4H_9{\cdot}CO{\cdot}NCS + C_6H_5{\cdot}NH_2 = C_4H_9{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_6H_5,$$

and reckoned on the amount of chloride used in the preparation of the thiocarbimide.

A sulphur determination afforded the following result.

0·2001 gave 0·1948 $BaSO_4$. S = 13·38.

$C_{12}H_{16}N_2SO$ requires S = 13·57 per cent.

The thiocarbamide is practically insoluble in boiling water, easily soluble in hot alcohol, rather sparingly in cold, freely so in ether, chloroform, carbon bisulphide, and benzene; from the latter it is partially precipitated by light petroleum. It also dissolves readily in cold concentrated sulphuric acid; the solution is precipitated on the addition of water. Ferric chloride produces no colour change; the solution is desulphurised by boiling with alkaline lead tartrate; with neutral silver nitrate, a white precipitate falls, which rapidly darkens; if the ammoniacal nitrate be used the mixture blackens at once.

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* For nomenclature, see this vol., p. 564.

Action of Caustic Alkali.—A portion of the thiocarbamide was dissolved in hot, dilute, caustic soda, and the solution, when cool, was precipitated by adding a slight excess of hydrochloric acid. The mixture was then boiled for a few minutes, until the odour of valeric acid was no longer perceptible, and a clear solution was obtained. On cooling, it deposited pure white prisms, easily soluble in hot water, sparingly in cold, soluble also in cold hydrochloric acid or caustic alkali, desulphurised by lead or silver salts, possessing an intensely bitter taste, and melting at 153—154°. From these properties, the compound was obviously phenylthiourea (m. p., 154°); its formation occurs as follows.

$$\mathrm{NHPh{\cdot}CS{\cdot}NH{\cdot}CO{\cdot}C_4H_9 + NaOH = C_4H_9{\cdot}COONa + CSN_2H_3Ph},$$

a reaction analogous to that observed in the case of succinyl-*ab*-diphenyldithiourea (*loc. cit.*, 568).

Action of Silver Nitrate.—Another portion, dissolved in hot spirit, was mixed with a little more than the theoretical quantity of silver nitrate Silver sulphide at once precipitated, and after a few minutes' boiling was filtered off; the filtrate, when concentrated, gave a crop of brownish crystals, which, on recrystallisation from dilute alcohol, were deposited in beautiful, colourless, silky needles, melting at 98—99° (corr.).

Analysis showed these to be the expected valerylphenylurea.

0·1984 gave 22·9 c.c of moist nitrogen at 23° and 740 mm. N = 12·94.

$\mathrm{C_{12}H_{16}N_2O_2}$ requires N = 12 76 per cent.

Valerylphenylurea is odourless, insoluble in cold water, almost indefinitely soluble in boiling alcohol, moderately so in cold. It is very freely soluble in ether, chloroform, benzene, and carbon bisulphide, easily in hot, and moderately in cold, light petroleum.

ab-*Valerylorthotolylthiocarbamide*, $\mathrm{C_4H_9{\cdot}CO{\cdot}N_4{\cdot}CS{\cdot}NH{\cdot}C_6H_4{\cdot}CH_3}$.

Prepared by adding the theoretical quantity of orthotoluidine, in alcohol, to a benzene solution of the thiocarbimide. Heat was evolved, and on concentration solid matter separated, amounting, when dry, to over 83 per cent. of the theoretical, reckoned as in the case of the corresponding phenyl-compound. By recrystallisation from spirit, the substance was obtained in large, well-formed, colourless, vitreous prisms melting at 142—143° (corr.).

0·2015 gave 0 1884 $\mathrm{BaSO_4}$. S = 12·85.

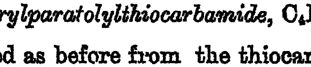
$\mathrm{C_{13}H_{18}N_2SO}$ requires S = 12·81 per cent.

Valerylorthotolylthiocarbamide is insoluble in boiling water, easily soluble in hot alcohol, sparingly in cold, very freely in chloroform, easily in carbon bisulphide, moderately in ether and benzene; soluble also in concentrated sulphuric acid, the solution being precipitated on diluting with water. The solution in spirit or alkali is desulphurised by boiling with alkaline lead tartrate. Ammoniacal silver nitrate desulphurises the solution instantly; the neutral nitrate gives a white precipitate, which rapidly decomposes with formation of silver sulphide.

Action of Caustic Alkali.—The compound dissolved readily in warm dilute caustic soda, and, on adding hydrochloric acid, a white, crystalline precipitate was formed, moderately easily soluble in boiling water (from which it was deposited in small prisms), sparingly soluble in cold, or in ether, and melting at the same temperature as *orthotolylthiourea*, namely, 160—161°.

Desulphurisation.—Formation of Valerylorthotolylurea.—A quantity of the thiocarbamide was desulphurised in boiling alcoholic solution, as described for the phenylic homologue; the solid product, after recrystallisation from spirit and animal charcoal, formed long, slender, silky white needles melting at 119—120° (corr.).

0·1996 gave 21·7 c.c. moist nitrogen at 23° and 740 mm. N = 12·19.



$CO<^{NH·C_6H_5}_{NH·CO·C_4H_9}$ requires N = 11·99 per cent.

The substance is practically insoluble in boiling water, very freely soluble in hot alcohol, chloroform, and benzene, moderately in ether and carbon bisulphide, somewhat sparingly in cold alcohol.

ab-*Valerylparatolylthiocarbamide*, $C_4H_9·CO·NH·CS·NH·C_6H_4·CH_3$.

Obtained as before from the thiocarbimide and paratoluidine, the yield being about 60 per cent. of the theoretical. When recrystallised from hot alcohol, it separated in brilliant, colourless prisms melting between 116° and 117° (corr.).

The formula was checked by a sulphur determination.

0·201 gave 0·189 $BaSO_4$. S = 12·92.

$C_{13}H_{18}N_2SO$ requires S = 12·81 per cent.

The paratolyl compound is insoluble in water, easily soluble in hot alcohol, sparingly in cold, very freely in chloroform, moderately in benzene. With sulphuric acid, silver and lead salts, it behaves like the corresponding ortho-derivative. By dissolving in warm dilute caustic alkali, and precipitating the solution with hydrochloric acid, *paratolylthiourea* was obtained in white prisms, melting at 187—188 (corr.).

ab-*Valeryl-α-naphthylthiocarbamide*, $C_4H_9{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_{10}H_7$.

Heat was evolved on mixing the benzene solution of valerylthiocarbimide with alcoholic α-naphthylamine, and, on cooling, solid matter separated, amounting, when dry, to 70 per cent. of the theoretical yield. By recrystallisation from spirit, using animal charcoal, slender, white needles were obtained, odourless, becoming somewhat electrical on friction, and melting at 129—130° (corr.).

0·2012 gave 0·1626 $BaSO_4$. S = 11·11.

$C_{16}H_{18}N_2SO$ requires S = 11·19 per cent.

The compound is insoluble in water, easily soluble in boiling alcohol, sparingly in cold. It is desulphurised by boiling with alkaline lead tartrate, with formation of a fine speculum; and the alcoholic solution gives, with neutral silver nitrate, a white precipitate, which soon begins to darken, or, with the ammonical nitrate, an immediate precipitate of silver sulphide.

Like its congeners, it dissolves readily in warm dilute caustic alkali; the solution, on cooling, deposits a solid, which crystallises from alcohol in white, rhombic prisms, difficultly soluble in boiling water, rather sparingly in alcohol, desulphurised by alkaline lead solution, melting at 196—197° (corr.), and consisting evidently of α-naphthylthiourea. M. p. of the latter, 198°.

n-*Valeryl-ν-benzylphenylthiourea*,*

$C_6H_5{\cdot}CH_2{\cdot}N(C_6H_5){\cdot}C(SH){:}N{\cdot}CO{\cdot}C_4H_9$.

Obtained, with evolution of heat, from the thiocarbimide and (alcoholic) benzylaniline; when recrystallised from spirit, it formed slender, pure white, odourless needles, melting at 125—126° (corr.).

0·2026 gave 0·1438 $BaSO_4$. S = 9·75.

$C_{19}H_{22}N_2SO$ requires S = 9·82 per cent.

The tertiary thiourea is insoluble in water, easily soluble in boiling alcohol, moderately in cold, soluble, also, in caustic alkali, from which it is reprecipitated unchanged on the addition of hydrochloric acid. [M. p. found, 125—126° (corr.); "unsymmetrical" benzylphenylthiourea melts at 136·5°.]

It differs, also, from the preceding acidic compounds in not being desulphurised by alkaline lead solution; moreover, when treated with neutral or ammoniacal nitrate of silver, a white precipitate falls, which does not blacken, even on boiling.

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* For nomenclature, see this vol., p. 565.

Valerylthiourea, $CSN_2H_3 \cdot CO \cdot C_4H_9$.

Alcoholic ammonia was added, in considerable excess, to the solution of valerylthiocarbimide; there was marked evolution of heat on mixing, and the liquid, when concentrated, deposited large, ice-like crystals, which were purified by recrystallisation from spirit, and analysed.

0·1308 gave 0·1877 $BaSO_4$. S = 19·72.
$C_6H_{12}N_2SO$ requires S = 20 01 per cent.

The recrystallised substance occurred in brilliant, vitreous prisms, devoid of odour, and melting, apparently without decomposition, at 158—159° (corr.). It is freely soluble in hot alcohol, benzene, and chloroform; moderately in hot water, cold alcohol, and ether; sparingly in cold water and cold benzene. With neutral silver nitrate, the solution yields a nearly white precipitate, slowly changing, through yellow and dull orange, to black; it is also readily desulphurised by warming with alkaline lead tartrate; ferric chloride produces no colour change.

Ethylic Valerylthiocarbamate (*Valeryl-β-thiourethane*), $C_4H_9 \cdot CO \cdot NH \cdot CS \cdot OC_2H_5$.

No perceptible evolution of heat occurred on mixing the thiocarbimide with a large excess of anhydrous ethylic alcohol, and, after a few days' standing, the mixture was concentrated on the water bath; the brownish, oily residue gradually deposited long needles, the whole eventually becoming almost solid. When collected with the aid of the pump, well pressed in bibulous paper, and recrystallised from acetone, the compound formed small prisms, faintly yellow when seen in mass, having a slight valerianic odour, and melting at 54—56°.

0·203 gave 0·2467 $BaSO_4$. S = 16·71.
$C_8H_{15}NSO_2$ requires S = 16·95 per cent.

It dissolves to a limited extent in boiling water, from which, on cooling, it separates as an oil; it is extremely soluble in the following liquids:—Methylic or ethylic alcohol, ether, acetone, ethylic acetate, chloroform, aldehyde, carbon bisulphide, benzene, cumene, and light petroleum. The alcoholic solution is slightly desulphurised* by treatment with alkaline lead tartrate; neutral or ammoniacal silver nitrate produces a white precipitate, which blackens on boiling.

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* Perhaps, owing to the presence of a trace of impurity; the odour, and the want of sharpness in melting point, also indicate that the compound was not quite pure

PART II.—*Derivatives of Cinnamoylthiocarbimide.*

Hitherto no acidylthiocarbimide derived from an "unsaturated" acid appears to be known: the following experiments relate to the preparation, in solution, of a member of the class in question and of its derivatives.

Cinnamoyl chloride, dissolved in anhydrous benzene, and dry lead thiocyanate, the latter in somewhat greater proportion than that required by the equation

$$2C_6H_5\cdot CH{:}CH\cdot COCl + Pb(SCN)_2 = 2C_6H_5\cdot CH{:}CH\cdot CO\cdot NCS + PbCl_2,$$

were heated together on the water bath, using a reflux condenser. The mixture gradually changed from pale yellow—its initial colour—to rather deep yellow, and after 10 minutes' boiling, the solution was found to be free from chlorine. After separating and washing the solid residue, the clear filtrate was diluted with benzene, as in the case of the valeryl compound. The solution thus obtained had a somewhat pungent odour, especially when warmed, resembling that of other acidylthiocarbimides, but less marked than usual. When mixed with alcohol and treated, in the cold, with ammoniacal silver nitrate, silver sulphide was precipitated almost instantly; the mixture was also readily desulphurised by warming with alkaline lead tartrate. Cold water decomposed the benzene solution only slowly when shaken up with it, the aqueous layer giving with ferric chloride a rather feeble reaction for thiocyanic acid; after warming, however, the iron salt produced a strong blood-red coloration, and a buff-coloured, amorphous precipitate was formed. On exposure for some time to (moist) air, pale yellowish crystals separated from the benzene solution; they were soluble in hot water, melted at 133°, and consisted of cinnamic acid.

ab-*Cinnamoylphenylthiocarbamide*, $C_6H_5\cdot CH{:}CH\cdot CO\cdot NH\cdot CS\cdot NH\cdot C_6H_5$.

Cinnamoylthiocarbimide and aniline were mixed in warm benzene solution; in about an hour, solid matter began to separate, and eventually the whole set to a solid crystalline mass. After draining off, washing, and drying, the yield was found to be 63 per cent. of the theoretical—reckoning from the chloride as starting point. By recrystallisation from boiling alcohol, the substance was obtained in felted masses of long, flexible, silky needles, melting, apparently without decomposition, at 165—166° (corr.).

A sulphur determination afforded the following result.

0·2 gave 0·1669 $BaSO_4$. S = 11·47.

$C_{16}H_{14}N_2SO$ requires S = 11·36 per cent.

Cinnamoylphenylthiocarbamide is insoluble in water, sparingly soluble in cold alcohol, benzene, and carbon bisulphide, with difficulty in boiling alcohol and ether, easily in chloroform, very freely in hot benzene. Its solution in caustic alkali is gradually desulphurised by boiling with alkaline lead tartrate; the alcoholic solution also gives up its sulphur on the addition of ammoniacal silver nitrate—slowly in the cold, or rapidly on heating.

Action of Silver Nitrate.—A boiling, somewhat dilute, alcoholic solution of the thiocarbamide, when treated with the above reagent, gave at once a precipitate of silver sulphide, and the filtrate from the latter, as it cooled, deposited *cinnamoylphenylurea*.

0·2076 gave 19·5 c.c. moist nitrogen at 16° and 746·5 mm. N = 10·73.

$CO<\begin{matrix}NH\cdot C_6H_5\\NH\cdot CO\cdot CH:CH\cdot C_6H_5\end{matrix}$ requires N = 10·55 per cent.

The urea crystallises from alcohol (in which it is difficultly soluble at the boiling point, and very sparingly in the cold) in microscopic white prisms, melting at 211—212° (corr.). It is insoluble in water or dilute alkali, rather difficultly soluble in boiling benzene, sparingly in ether, carbon bisulphide, and cold benzene.

ab-*Cinnamoylorthotolylthiocarbamide*,
$C_6H_5\cdot CH:CH\cdot CO\cdot NH\cdot CS\cdot NH\cdot C_6H_4\cdot CH_3$.

Prepared, like the corresponding phenyl derivative, from cinnamoylthiocarbimide and orthotoluidine; it formed whitish needles, the yield of which, calculated as before, amounted to only 34 per cent. of the theoretical. By recrystallisation from alcohol, the compound was obtained in nearly white needles, having a faint yellowish tinge, and melting, at 182—183° (corr.), to a pale green liquid.

0·2002 gave 0·1582 $BaSO_4$. S = 10·86.

$C_{17}H_{16}N_2SO$ requires S = 10·82 per cent.

It is insoluble in water, only moderately soluble in boiling alcohol or ether, easily in hot benzene and in chloroform. It dissolves also in hot dilute, caustic potash; the solution thus obtained is precipitated by hydrochloric acid, and is gradually desulphurised by boiling with alkaline lead tartrate. The alcoholic solution gives with either neutral or ammoniacal silver nitrate a whitish precipitate, which darkens slowly in the cold, or blackens at once on heating.

ab-*Cinnamoylparatolylthiocarbamide*,
$C_6H_5\cdot CH:CH\cdot CO\cdot NH\cdot CS\cdot NH\cdot C_6H_4\cdot CH_3$.

The constituents were mixed in slightly warm benzene solution, and in a few minutes yellow needles began to separate; after being drained, washed with more benzene, and dried, the yield amounted to about 40 per cent. of the theoretical. By recrystallisation from boiling alcohol, beautiful, hair-like needles were obtained, having a faint lemon-yellow tinge, and melting at 194—194.5° (corr.). The formula was verified by a sulphur determination.

0·2017 gave 0·1614 $BaSO_4$. S = 11·00.

$C_{17}H_{16}N_2SO$ requires S = 10.82 per cent.

The compound is insoluble in boiling water, sparingly soluble in boiling alcohol, nearly insoluble in cold, moderately in hot benzene, difficultly in ether and carbon bisulphide. It scarcely dissolves in hot dilute caustic alkali, but is soluble, with decomposition, if the alkali is concentrated. Alkaline lead tartrate desulphurises it slowly, and with some difficulty, but the sulphur is easily withdrawn, even in the cold, by neutral or ammoniacal nitrate of silver.

ab-*Cinnamoyl-α-naphthylthiocarbamide*, $C_6H_5 \cdot CH{:}CH \cdot CO \cdot NH \cdot CS \cdot NH \cdot C_{10}H_7$.

α-Naphthylamine and the thiocarbimide were mixed, as before. Heat was liberated, and the contents of the vessel solidified at once, owing to the separation of a yellowish, finely divided substance, the yield of which, when dry, was found to be nearly 60 per cent. of the theoretical. The product was recrystallised from hot benzene, and thus obtained in felted masses of long, very slender, flexible needles melting between 203—204° (corr.).

It is insoluble in water, very sparingly soluble in hot alcohol and ether, or in carbon bisulphide, rather sparingly in chloroform and hot benzene, almost insoluble in cold, somewhat more easily in boiling toluene.

0·2141 gave 0·1482 $BaSO_4$. S = 9·51.

$C_{20}H_{16}N_2SO$ requires S = 9.65 per cent

Cinnamoylthiourea, $CSN_2H_3 \cdot CO \cdot CH{:}CH \cdot C_6H_5$.

Excess of alcoholic ammonia was added to a warm benzene solution of the acid thiocarbimide; considerable evolution of heat occurred, and solid matter at once separated, consisting of silvery-grey, microscopic crystals. These were dissolved in boiling alcohol, which, on cooling, deposited long, slender, flexible, white needles melting at 215—216° (corr.).

0·2008 gave 0·228 $BaSO_4$. S = 15·61.

$C_{10}H_{10}N_2SO$ requires S = 15·55 per cent.

Cinnamoylthiourea is insoluble in water, only moderately soluble in boiling alcohol. and very sparingly in cold. The alcoholic solution is desulphurised, but not readily, by boiling with alkaline lead tartrate; with either neutral or ammoniacal silver nitrate, desulphurisation occurs moderately easily in the cold, or copiously and rapidly on warming.

Ethylic Cinnamoylthiocarbamate (Cinnamoyl-β-thiourethane), $C_6H_5\cdot CH{:}CH\cdot CO\cdot NH\cdot CS\cdot OC_2H_5$.

The thiocarbimide, in benzene, was mixed with a considerable excess of absolute ethylic alcohol; no perceptible evolution of heat occurred, and the mixture, after five days, still remained clear. The excess of alcohol was then carefully driven off on the water bath, and a brownish liquid thus obtained, which, later on, deposited yellow needles; these, when collected and recrystallised from spirit, were pale yellow, and melted at 134—135° (corr.).

0·2002 afforded 0·2001 $BaSO_4$. S = 13·74.

$C_{12}H_{13}NSO_2$ requires S = 13·63 per cent.

The thiourethane is insoluble in water, easily soluble in hot alcohol, moderately in cold. Its solution is scarcely perceptibly desulphurised by treatment with alkaline lead tartrate, and yields, on the addition of ammoniacal silver nitrate, a yellowish-white precipitate, which does not blacken, even when the mixture is boiled.

It is intended to continue these experiments with lead thiocyanate, so as to include chlorides other than those containing the group —CO·Cl; for example, picryl chloride, phenylsulphonic chloride, and the chlorides of the alkylsulphuric acids.

The author wishes to express his thanks to Mr. R. E. Doran for the assistance which he has given in connection with the experimental work recorded in the present paper.

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CX.—*On Flame Temperatures and the Acetylene Theory of Luminous Hydrocarbon Flames.*

By Arthur Smithells, B.Sc.

In a paper read before the Chemical Society in 1892 (Trans., **61**, 217) I gave a short summary of the evidence bearing upon the structure of luminous hydrocarbon flames, and endeavoured to account for the four distinctive parts of such flames which had been generally recognised by workers on this subject. Referring to the separation of solid particles of carbon, I said, "a problem remaining to be studied concerns the exact course of the decomposition of the hydrocarbon in the flame."

Shortly after the above paper appeared, Professor Lewes read a paper before the Society (Trans., 1892, **61**, 322), in which he advanced the doctrine that the luminosity of flame depends on the intermediate formation of acetylene. He also adopted a new view as to the zones which constitute an ordinary luminous flame In subsequent papers (*Proc. Roy. Soc*, 1894, **55**, 90; 1895, **57**, 394, 450), Professor Lewes has developed his theory concerning the source of the luminosity in hydrocarbon flames.

He recognises three distinct parts in luminous flames:

1. "The inner zone, in which the temperature rises from a comparatively low point at the mouth of the burner to between 1000° and 1100° at the apex of the zone." In this zone, the most important action is the conversion of part of the hydrocarbons into acetylene.

2. "The luminous zone, in which the temperature ranges from 1100° to a little over 1300°." Here the chief action is the decomposition into its elements of the acetylene formed in the preceding zone.

3. "The extreme outer zone, in which the cooling and diluting influence of the entering air renders a thin layer non-luminous, and finally extinguishes it"

In advancing this view, Professor Lewes omits all notice of the detailed experimental evidence (Trans., 1892, **61**, 217) by which I was led to endorse and amplify the older view as to the distinctive parts of a flame. I do not feel it necessary at present, therefore, to say more as to the latter, but will confine myself to a categorical consideration of the evidence on which the acetylene theory is based.

The Temperature Gradients of Flame.

In his first paper (Trans., *loc. cit.*), Professor Lewes says that the Le Chatelier thermo-couple "gives a means of measuring the temperature of flames with ease and comparative accuracy." In a paper published in the *Philosophical Magazine*, 1894, [5], **37**, 245, I have adverted at length to the vagueness of the term temperature as applied to flames, and to the impossibility of obtaining any accurate measurement of the temperature of the exceedingly thin sheets of glowing gases (or solid particles) of which flames are composed. Though Professor Lewes, in his last paper (*Proc. Roy. Soc*, 1895, **57**, 450), seems to accept and to utilise these views, and in some measure to strengthen them, he still adduces measurements of temperature as the chief basis for his theory. I have therefore made a number of experiments on the subject, with the results described in the following paragraphs.

The instrument which I have employed for the measurement of flame temperatures is the platinum and platinum-rhodium thermocouple, which has also been used by Professor Lewes in his experiments on flame; this instrument has the advantage that it can be made of thin wires, which can be so bent that a considerable length of wire on each side of the junction can be placed in the sheath of flame in which the measurement is being made, and thus the drain of heat from the junction by conduction considerably reduced.

The junction was made by singly linking the wires and then welding them. Since the couple will obviously register the lowest temperature on the surface of contact of the two metals, it is desirable to keep that surface as small as possible, and hence the junction made as above was preferred to a twist of the two wires.

The wires of the thermo-couple had a diameter of 0·5 mm., and were connected by copper wires (the junctions being immersed in water) to a reflecting galvanometer, the total resistance being about 4 ohms. Calibration was effected by means of boiling sulphur (448°) and melting salt (775°). I adopted the statement of Le Chatelier that the curve connecting E.M.F. and temperature is, between these limits, a straight line, and assumed that this might be produced even to the temperatures measured. The resistance of the circuit was not high enough to be unaffected by changes of temperature in the region of the junction, but as both the increase of resistance and the increase of E.M.F. are proportional to the temperature, the curve compounded of these two changes should still be a straight line, the slope of which was determined in the calibration. Incidentally, in the use of the couple, the assumptions made were sufficiently justified by the melting point of the platinum wire being determined as 1830 by fusion in a hydrogen flame. (The number given by Violle is 1775°.)

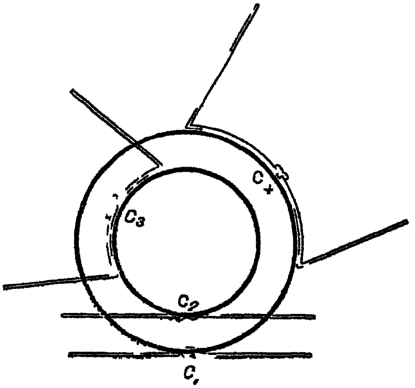
Non-luminous Hydrocarbon Flames.—It will be convenient in the first place to record the observations made in a Bunsen flame, using coal gas. When the air supply to such a flame is plentiful, a very distinct differentiation into two cones is noticeable. The flame is thus comparatively simple, but it serves admirably to exhibit the precautions that have to be observed in making measurements which shall indicate, even comparatively, the average temperature of the region in which the junction is immersed, and the caution necessary in drawing conclusions from such measurements.

Stretching the two wires of the thermo-couple straight, and immersing the couple in the region of the flame where a measurement was desired, an approximately uniform temperature (1517° to

1542°)[*] was recorded at all points laterally from the inner cone to the outer cone.

But it is obvious that when the couple is used in the manner described no valid measurements are possible. Fig. 1 represents a horizontal section through the lower half of a Bunsen flame (the concentric circles representing the two cones), showing also the disposition of the thermocouple. In the position C_1 the junction is heated solely at the point of immersion in the outer cone. In the position C_2 it is heated by immersion in the inner cone, but since the wires pass on each side through the outer cone as well, there is here a second supply of heat which makes the reading relatively too high. This error can be eliminated to a large extent by bending the wires so as to fit the form of the cones (C_3 and C_4 in the figure); a considerable length on each side of the junction is thus immersed, and loss of heat by conduction avoided in both cases. Adopting this arrangement, it was found that the couple registered a temperature of 1611°, or 80° higher in the outer cone at C_4 than in the inner one at C_3; the average temperature of the outer cone is, in fact, considerably higher than that of the inner one. This result is not incompatible with the statement I have previously made (Trans., 1892, 61, 204) to the effect that when the cones are widely separated the inner one has the higher temperature. The apparent contradiction is explained by the simple consideration that in a Bunsen flame, where the cones are close together, the combustible gases passing from the inner cone have not time to radiate much heat before burning, and consequently to the heat developed by their actual combustion in the outer zone must be added that which they bring with them.

FIG. 1



The above experiments, therefore, show two things: First, the fallacious results that may be obtained by not disposing the couple with due regard to the conformation of the zone of flame to be measured; and secondly, the difficulty of ascertaining the increase of temperature contributed by the chemical changes occurring in any one spot. I have made no attempts to measure the temperatures in the region of no combustion which lies within the inner cone; such measurements, even if made by thrusting the couple upwards through the burner tube would be useless as a means of determining the temperature of the gases, as the stationary couple would obviously be heated to a much higher temperature than the stream of gases, by the heat radiated from the walls of flame which surrounded it. Besides this, there is always the likelihood of slow combustion being induced at the surface of the platinum.

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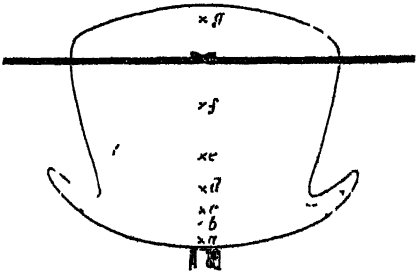
[*] As will be explained subsequently, no importance is attached to these temperatures as *absolute* temperatures.

Luminous Coal Gas Flames.—The flame experimented upon was that given by No. 4 Bray's union jet at a gas pressure of about 2½ in. of water. The flame had the form given in the diagram, Fig. 2.

FIG. 2.



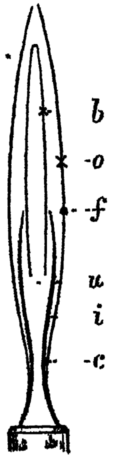
To obtain any useful measurements in this case, as in the other, the wires on each side of the couple must be placed in zones of the same temperature as the junction. This may be done approximately by laying the junction and the adjacent wires in a horizontal straight line, and introducing it along the flat face of the flame so that it may be placed with a considerable length of the wires immersed symmetrically in any one sheath and passing through parts of the flame in like condition.

When the couple arranged in this way was brought up to the flame and passed through it, the readings showed that the flame was invested by a non-luminous sheet of active combustion, in which the temperature was a maximum. At the position *f*, for example (Fig. 2), a maximum temperature of 1613° was registered, about 3 mm. outside the luminous sheet. Proceeding inwards, the temperature fell to 1463° at the luminous sheet, and within the sheet (that is, between the two luminous walls) to 1100°, the fall afterwards continuing to about 700° as the soot deposit on the couple grew in thickness. The sheath of high temperature invests the whole flame, but, as we should expect, varies somewhat in apparent thickness. At the position *a* (quite close to the burner), a temperature of 1478° was recorded on the sheath, and 196° within; at *b*, 1564° and 382°; at *c*, 1560° and 641°; at *d*, 1547° and 947°; at *e*, 1576° and 1110°; and at *g*, where the sheets from either side coalesced, 1613°.

The measurements for the inner parts of the flame given above have only a negative significance. It is obvious that they cannot be true temperatures, inasmuch as the wires have always to pass through the hot outer sheath of flame, and, moreover, the couple would attain by radiation from the outer walls a higher temperature than the rapid stream of gas in which it was immersed. The readings are not even comparable, as the flame varies in breadth and thickness from point to point in a vertical plane. All that can be said is that the readings give no evidence of any sudden thermal change occurring in the space enclosed by the mantle, and that they are in no wise opposed to the view that the stream of gas surrounded by the mantle is steadily heated as it ascends. The recorded temperatures of the mantle are less open to objection, but are still far from being accurate. As just given, they show a slight increase as the flame is ascended. But such an effect might result not from a real difference of temperature but from a difference in the thickness of the sheath. This is, in fact, the case. It was found that a platinum wire of 0·1 mm. diameter could easily be melted in the mantle at the points *a*, *b*, and *c*. It could be melted at *f* only at a distance of 3 mm outwards from the luminous sheet, and at *e* it did not fuse in any position.

These results give a temperature slope opposite to that indicated by the thermo-couple. The explanation is, however, very simple, and will be readily seen on reference to Fig. 3. At the position *c*, the platinum wire is at a point corresponding to the lower part of a Bunsen flame where the cones are close together. At *f* it is on what

FIG 3.—Diagrammatic vertical section of coal-gas flame from union jet (Compare Fig 2.)



i, inner blue layer } forming together the non-luminous sheath
o, outer lilac layer }

u, unburnt gas.

l, luminous sheet

corresponds to the outer cone at a point much higher in a Bunsen flame. A very small shift inwards will, in the first case, put the wire into the region of unburnt gas, and in the second case bring it into a space filled with products of partial combustion, which, though very hot, will burn at *f*, producing a much higher temperature, as already shown. At the tip of the flame, the constant movements render it impossible to discover a sharp surface of high temperature and to keep the thin wire in it.

In the thermo-couple we have an instrument which is gross compared with the fine platinum wire. At *e*, it is not thoroughly immersed owing to the thinness of the sheath, whilst at *f* and at the tip of the flame it is wholly immersed in the heated gases from the lower parts of the flame. Hence it registers a higher temperature in the last two cases.

Similar results were obtained with other flames, showing in each case the existence of an external sheath of maximum temperature. It is, perhaps, worth noting that when hydrogen is burnt from a flat-flame burner, it is possible to melt in it a platinum wire which is quite unaffected in a flame of hydrogen produced at low pressure on the end of a tube of circular section. The pressure at which the gas issues in the first case ensures a rapid admixture with air and the consequent formation of a sheath of flame, which is sharply defined and of appreciable thickness. In the second case, the sheath is much more vague.

The chief conclusions which I desire to establish from the experiments described in this part of the paper are as follows :—

1. There are two chief temperature gradients in a luminous coal gas flame; one on a vertical axis in the region of unburnt gases, which is in all probability a steady decline from the top to the bottom; the second on a horizontal axis, showing as we proceed from the centre of the unburnt gas a steep ascent to the point of contact with the luminous sheath, then a still steeper ascent to the point of contact with the mantle where the highest point is abruptly attained.

2. The temperature of the mantle of a coal-gas flame is above the melting point of platinum, and cannot therefore be determined by a thermo-couple in which this metal is one element.

3. The measurement of the average temperature of a flame is impracticable, and statements involving the expression can have no scientific meaning.

An inspection of the foregoing results shows as forcibly as could be wished how vague and misleading it is to speak of the temperature of any part of a flame without recording precisely how the measurement has been made. They show, also, that the sudden temperature changes in a flame are found, not in a vertical, but in a horizontal plane, and consequently Professor Lewes's measurements, which relate almost exclusively to points at different heights in the flame, do not afford a satisfactory basis either for mapping the flame into zones, or for any hypothesis as to the cause of luminosity. But the results obtained by a careful use of the thermo-couple go much further than this. They show that the part of a flame which Professor Lewes describes as "the extreme outer zone in which the cooling and diluting influence of the entering air renders a thin layer non-luminous and finally extinguishes it," is in reality the very hottest part of a flame; and, further, they do not show a sudden increase of temperature at any point in the vertical plane such as might be expected to arise when a stream of acetylene passing upwards reached the point at which the temperature was sufficient to effect its resolution into carbon and hydrogen with the disengagement of an enormous quantity of heat. The measurements, in fact, are not favourable to the acetylene theory, but the reverse.

On the other hand, the results obtained are entirely in harmony with the views I have previously expressed (Trans., 1892, 61, 217). I endeavoured to demonstrate that the bright blue calyx and the lilac mantle of a luminous hydrocarbon flame are essentially of the same character as the two cones of a Bunsen flame.* The temperature measurements support this view, and show that this outer sheath is really a region where the combustible gas is mixed with air sufficiently to produce a high temperature non-luminous combustion. The luminous flame must therefore be regarded as invested by a sheath of gas in active "non-luminous" combustion, and the stream of gas within this sheath is naturally the more heated the higher it ascends.

Another point to which I desire to draw attention is, that in a luminous flame it is incorrect to indicate the luminosity as commencing suddenly at a certain height. A moment's inspection of a candle flame will show that the luminosity begins even below the top of the wick, and increases steadily to a maximum intensity as we proceed upwards, after which it again fades. It is also incorrect to regard the inner (non-luminous) zone as ending a short distance above the wick or burner where, as a matter of fact, to the eye it appears to end. If the image of the sun be focussed on a luminous flame where the light is brightest and where the luminosity seems to extend right through the core of gases, it will be seen, by the double image produced, that there, as elsewhere, the glowing particles constitute an extremely thin sheet, and, that so far as luminosity is concerned, the flame is hollow from bottom to top. The luminosity, in fact, is developed in a candle flame, except for a negligible distance at the base, over the whole of the flame, and the luminous portion is a sheath of carbon particles lying within the non-luminous investing sheath, and taking a glow which accords strictly with the view of the genesis of a flame that I have elsewhere laid down.

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* An important piece of evidence as to the nature of the blue calyx to which I did not allude in the paper referred to, is afforded by the spectroscope. It is this part of a luminous flame, and this part only, which gives the "carbon" spectrum, and as is well known, the same spectrum is given by the inner cone only of a Bunsen flame.

If any further evidence were required as to the uncertainty attaching to temperature measurements in flames, it might be found in Professor Lewes's own papers. Thus, for a coal-gas flame we have in two separate papers the following two sets of measurements.

	'Proc. Roy. Soc.,' 1895.	'Trans. Chem. Soc.,' 1892.
Non-luminous zone..........	1023°	1014°
Commencement of luminosity zone	1658	1267
Near top of luminous zone....	2116	1368

It is true that the flames were not of the same size, and therefore the readings might be different, yet we should reasonably expect them to show something like parallelism. It may also be noted that although Professor Lewes thinks that his figures may be from 100° to 200° too low, one of the temperatures recorded is 100° higher than Deville's, and 330° higher than Violle's, melting point of platinum—a metal which is one element in the thermo-couple itself.

The Occurrence of Acetylene in Flames.

The origin of the acetylene theory appears to lie in the observation made by Professor Lewes, that this gas is found among the mixture of gases aspirated from a luminous gas flame. This is quite in accordance with my own previously recorded experience (Trans., 1892, 61, 215), and it is, indeed, quite in accordance with general principles that in a region in which hydrocarbons are being subjected to a high temperature there should be a tendency for the formation of the highly endothermic acetylene. But to say that over 80 per cent. of the unsaturated hydrocarbons present when luminosity commences is acetylene, is likely to give a very false impression as to the importance to be attached to the presence of this gas. The statement is in accord with Professor Lewes's published analysis, but it should be borne in mind that the total amount of unsaturated hydrocarbons is only 1·98 per cent., and that the absolute amount of acetylene is therefore 1·41 per cent. Thus the gas which the flame has elaborated, and which, according to Professor Lewes, is its luminous essence, is a mixture of about 1·5 parts of acetylene and 0·5 of other unsaturated hydrocarbons with 98 parts of other gases, more than four-fifths of which are actually incombustible. I am at a loss to understand how such a mixture can be supposed to have the properties attributed to it by Professor Lewes.

The Comparison of Different Flames.

Professor Lewes states that the luminosity of two flames of given size, burning from the same jet, should (apart from the acetylene theory) be governed by (*a*) the temperature of the flames, (*b*) the number of carbon particles in a given area.* Subsequently, he lays much stress on the statement that, whilst ethylene and acetylene contain an equal number of carbon atoms in the molecule, and the flame of the former is hotter than that of the latter, yet the acetylene flame is much more luminous.

Such an argument would, no doubt, have weight if we might regard the two flames as chemically similar. But this is far from being the case. If we are to decide *à priori* what will be the relative number of carbon particles in the flames of two hydrocarbons, we have not only to consider the formulæ of the gases, but likewise their diffusibility and inflammability, and the steps in their combustion which gives the particular conformation to their flames; the conditions, indeed, are so complex as to invalidate all theoretical predictions as to the total number of carbon particles. How it can be supposed that anyone will regard two flames as fairly comparable when burning from the same jet is difficult to understand, seeing that it is perfectly well known, and has been much insisted on by Professor Lewes himself, that different burners are required to develop the full illuminating value of each particular hydrocarbon. In the face of this fact, it is hardly credible that anyone would grant the assumption, so lightly made, as to the relation between the total number of carbon particles in a flame and the formula of the hydrocarbon.

Professor Lewes also speaks of the temperature of a flame as if it were a simple property capable of expression in a simple way, ignoring the fact that the temperature within a flame varies by hundreds of degrees at intervals of a few millimetres, and that the distribution of temperature zones in a flame has a special character for each hydrocarbon.

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* The word "area," judging by the context, is used here, as elsewhere, in the paper to mean volume.

The Flame of Acetylene.

Great stress is laid by Professor Lewes on the evidence deduced by him from observations on the acetylene flame. This flame is undoubtedly possessed of extraordinary luminosity, and if the measurements of its temperature, recorded by Professor Lewes, were valid, there might be some reason to seek for a new theory of luminosity. I am, however, unable to accept these measurements as representing the temperature of the flame, and I cannot understand on what system they have been made. According to Professor Lewes, the acetylene flame is characterised as much by its low temperature as by its high luminosity, yet observations I have made show that, like other hydrocarbon flames, it is surrounded by a non-luminous sheath of maximum temperature, and this sheath is so hot that the platinum limb of a thermo-couple, which had withstood the highest temperatures of the coal-gas flame, melted when introduced into it. This is not difficult to understand, since here we have not only the heat of combustion of carbon and hydrogen to reckon with, but also the large amount of heat of decomposition of the acetylene molecules. This sheet of high temperature surrounds the whole of the acetylene flame, and there is thus no cause for surprise at its high illuminating effect. It is exactly what we should expect from a flame consisting of a sheath of exceedingly high temperature enclosing a gas unusually rich in carbon and easily split up by heat. If we suppose the acetylene to be decomposed, within the flame, on the surface of contact of the non-luminous sheath and the zone of unburnt gas, there would be a densely crowded sheet of carbon particles heated to an extremely high temperature, a state of things which *must* result in a high luminous effect, and I am not aware of any grounds for supposing that this is not a perfectly adequate explanation of the marked illuminating value of the acetylene flame. The introduction of a platinum wire into the external non-luminous sheath of an acetylene flame shows at once that, contrary to Professor Lewes's explicit statement, the temperature of the flame, due to combustion, is perfectly adequate to produce a glow not less bright than that actually shown by the carbon particles.

Thermochemical Considerations.

Professor Lewes maintains from his observation that the flame of acetylene is characterised by low temperature, and that consequently some fresh theory is required to account for the high luminosity of the carbon liberated within it. To obtain such a theory he has recourse to thermochemical considerations which are, I believe, both uncalled for and incorrect.

He first alludes to the highly endothermic character of acetylene, and to the fact that when this gas is decomposed by heat the carbon is luminous at the moment of separation This decomposition, even when occurring in flames, he regards as taking place "with a rapidity almost akin to detonation," the heat evolved being confined to the liberated products. It is thus possible to have a highly luminous flame of low "average temperature."

Now, in an acetylene flame we are dealing, according to Professor Lewes, with acetylene in the act of burning, and acetylene in the act of separating into its elements. The latter process, he states, is calculated to produce a temperature of over 6000°; the former gives a calculated temperature above 3000°; it is, therefore, difficult to see how a flame made up in this way could possess a low average temperature. It surely is not supposed, because acetylene decomposes "with a rapidity almost akin to detonation," that the thermal effect of this operation occurring continuously in the flame is incapable of being detected by the thermo-couple.

It appears to me that the only circumstances where the argument at first sight seems applicable, would be where a flame of a hydrocarbon burning with a low average temperature contained a comparatively sparse supply of acetylene molecules. If these sparsely distributed molecules were supposed to undergo decomposition, and the heat to be localised in the liberated carbon and hydrogen, then there might be a number of *loci* of extremely high temperature which would have little effect on the general average. But such an argument would only hold good for explaining abnormally high luminosity if the source of light were gaseous carbon. If this view is excluded, and the luminosity attributed to carbon *particles*, then to form these particles the coalescence of the liberated atoms is essential, and before this coalescence could be effected between atoms which are *ex hypothesi* widely separated, they would inevitably have departed far from their original unique condition of temperature by encounters with the foreign molecules among which they are dispersed.

Professor Lewes says, "the supporters of the 'solid particle' theory of luminosity agree in concluding that the liberated carbon, existing as it does in a state of molecular division, is heated to incandescence." I am quite unable to understand the meaning of these words. Is the expression "a solid body in a state of molecular division" to be taken as a periphrasis for the word *gas?* If it is, these words sound the keynote of much that follows in the paper, for, whilst throughout he continues to speak of solid particles of carbon as the source of light in hydrocarbon flames, his theoretical speculations are applicable only to atoms.

The Alleged Liberation of Carbon from Cyanogen in Flames.

Among the indirect evidence which Professor Lewes adduces in support of his theory is an observation with respect to the behaviour of cyanogen which, if correct, would be interesting and perhaps of importance. He points out that this gas is more highly endothermic than acetylene, and argues that, if raised to a sufficient temperature, it should be resolved into its elements with a not less striking luminous effect than that seen with acetylene. He then describes an experiment in which a jet of cyanogen is sent up into a hydrogen flame, "with the result that the flame at once became luminous, and on surrounding the hydrogen flame with an atmosphere of oxygen to increase the temperature the luminosity was considerably increased." I repeated this experiment precisely according to Professor Lewes's statement. A yellow luminosity was at once noticed, and it is true that it is not unlike what might arise from a sparse supply of carbon particles, but on placing a cold piece of porcelain in the flame no trace of a deposit of carbon was obtainable. This fact, together with the hue of the flame, suggested the idea that the luminosity might be due to the formation of ammonia by the action of the hydrogen on the cyanogen. This turned out to be the case. Substituting a jet of ammonia for one of cyanogen in the experiment, a similar luminosity was obtained, and on arranging a double apparatus, one being cyanogen with hydrogen, and the other ammonia with hydrogen, and observing the spectra of the two flames simultaneously in the field of view of a spectroscope, I found a complete coincidence of the lines and bands. The substitution of an atmosphere of oxygen for one of air certainly caused a brighter appearance, but this was mainly due to the glow of the platinum orifice and to the introduction of more sodium into the flame. As a matter of fact, the oxygen suppresses the formation of ammonia, and the cyanogen burns with a flame giving its characteristic spectrum, though slightly brighter than in air.

The arguments deduced by Professor Lewes from the behaviour of cyanogen therefore are invalid, and instead of forming a support for the acetylene theory, the evidence deduced from the behaviour of this gas is, if anything, antagonistic to the theory.

I subjoin a statement of the chief conclusions arrived at in this paper, in addition to those enumerated on p. 1055.

1. The description of the structure of a flame adopted by Professor Lewes is not in harmony with the facts.

2. There is no evidence of more than a very small percentage of acetylene at any point within an ordinary luminous flame (the acety-

lene flame itself alone excepted) and the acetylene that is formed is associated with so large a quantity of other gases that there is no reason for supposing that it is of primary importance in the emission of light.

3. There is no evidence of any local condition of temperature within the flame such as would point to the decomposition of acetylene with the evolution of much heat.

4. The mapping of flames adopted by Professor Lewes is based on temperature measurements which are erroneous and of no valid applicability for the purpose in view.

5. The conclusion in favour of the acetylene theory based on the comparative luminosity of the ethylene and acetylene flames is due to a neglect of the consideration that in the latter there are higher temperatures and a greater relative amount of carbon.

6. The indirect evidence deduced from the behaviour of cyanogen arises from the yellow ammonia flame having been mistaken for one containing solid carbon.

7. The theoretical arguments based on thermochemical considerations are invalid.

8. The phenomena of luminous hydrocarbon flames can be adequately explained without the acetylene theory.

If the criticism which I have offered is just, then the acetylene theory of luminosity will share the fate of the "dense hydrocarbon" theory. We know that all hydrocarbons in contact with hot surfaces deposit carbon, and this is what occurs in their flames. What else is produced as the carbon is deposited is, I think, after all a problem of comparatively little interest. I have previously indicated one way in which it might be attacked (Trans., 1892, 51, 217), but I have found the experimental difficulties practically insurmountable. Our means of analysis are quite insufficient to deal either qualitatively or quantitatively with gases containing a very small percentage of an unknown number of hydrocarbons, many, it may be, belonging to the same homologous series. The solution of this problem must, I fear, be delayed for a very long time.

In connection with this paper I have received most valuable assistance from Mr. G. R. Thompson, B.Sc., to whom I here desire to acknowledge my indebtedness.

The Yorkshire College,
Leeds.

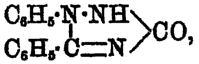
CXI.—*Synthesis of Diphenyloxytriazole.**

By George Young, Ph.D., Firth College, Sheffield.

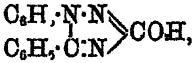
In a preliminary notice previously communicated to the Society (Proc., 1894–95, 124), I described a reaction which resulted in the formation of 1 : 5-diphenyl-3-oxy-1 : 2 : 4-triazole. This substance is produced by the action of an oxidising agent on a mixture of benzaldehyde and α-phenylsemicarbazide, and its formation may be represented by the equation—

$$C_7H_9N_3O + C_7H_6O + O = C_{14}H_{11}N_3O + 2H_2O.$$

The product is a white crystalline substance which dissolves in warm concentrated hydrochloric acid and in dilute alkalis. Its alkaline solution has no action on Fehling's solution even on prolonged boiling. Heated with phosphorus pentasulphide, it undergoes Andreocci's reaction for oxytriazoles, being reduced to a weak base of the formula $C_{14}H_{11}N_3$. Its constitution must be either—

I. 

$$\begin{matrix} C_6H_5\cdot N\cdot NH \\ | \\ C_6H_5\cdot C{=\!=}N \end{matrix} > CO,$$

or II. 

$$\begin{matrix} C_6H_5\cdot N\cdot N \\ | \\ C_6H_5\cdot C{:}N \end{matrix} \gg COH,$$

and the pronounced acid and extremely feeble basic character of the substance would seem to make Formula II the more probable.

As the 2 mols. of water formed in the reaction are different in their origin—the oxygen atom for the one molecule being supplied by the benzaldehyde, that for the other by the oxidising agent—it seemed probable that the action would take place in two stages. Some preliminary experiments showed that, if the conditions at all approach those under which the formation of the diphenyloxytriazole takes place, benzaldehyde and phenylsemicarbazide have, when all oxidising agents are carefully excluded, no action on each other. The intermediate product could therefore not be a benzylidene derivative of phenylsemicarbazide, and the action is not, as was first supposed, analogous to that by which Bladin (*Ber.*, 1889, 22, 796) prepared diphenylcyanotriazole from phenylhydrazine dicyanide and benzaldehyde. The first stage then must be an oxidation process. It might possibly have resulted in the formation of

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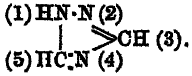
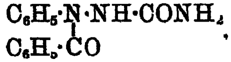
* The name triazole was given to the carbon nitrogen ring, $C_2N_3H_3$, by Bladin, who first described derivatives of it, and his nomenclature is adhered to in this paper, the position of substituting groups and the relative positions of the nitrogen atoms in the ring being shown according to the plan



$$\begin{matrix} (1)\,HN\cdot N\,(2) \\ | \\ (5)\,HC{:}N\,(4) \end{matrix} \gg CH\,(3).$$

a benzoylphenylsemicarbazide,  $\begin{array}{l}C_6H_5{\cdot}N{\cdot}NH{\cdot}CONH_2\\ C_6H_5{\cdot}CO\end{array}$, which, loosing water in the second stage, would form the triazole ring; but this substance, when prepared by Widman (*Ber.*, 1893, **26**, 948) from benzoyl chloride and phenylsemicarbazide, resisted all inducements to the ring condensation. The failure of an attempt to produce the final product by the action of benzoic acid on phenylsemicarbazide, shut out the possibility that the first stage might consist in oxidation of the benzaldehyde. A more successful result was obtained by excluding the benzaldehyde from the first stage; the action then took place according to the equation—

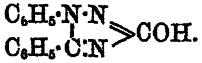
$$C_7H_9N_3O + O = C_7H_7N_3O + H_2O,$$

the product being phenylazocarbamide, $C_6H_5N{:}N{\cdot}CONH_2$. This, when heated in alcoholic solution with benzaldehyde, condenses with it to diphenyloxytriazole.

$$C_7H_7N_3O + C_7H_6O = C_{14}H_{11}N_3O + H_2O.$$

These two equations represent the two stages of the reaction. It is true the condensation in the second stage takes place with more difficulty (see experimental details) when the intermediate product is first isolated, than when the two stages are allowed to proceed together; the ease with which the second stage takes place under the latter condition is probably due to the amount of heat which is evolved by the oxidation.

EXPERIMENTAL.

1 : 5-*Diphenyl-3-oxy-1 : 2 : 4-triazole*,  $\begin{array}{l}C_6H_5{\cdot}N{\cdot}N\\ C_6H_5{\cdot}C{:}N\end{array}\!\!>COH.$

An alcoholic solution of benzaldehyde and phenylsemicarbazide was boiled for a few minutes, the alcohol evaporated over the water bath, and the residue extracted with boiling water to remove unchanged phenylsemicarbazide; the white, crystalline residue was purified by recrystallisation from alcohol. The long, white needles thus obtained, on analysis, gave figures agreeing with those required for the formula $C_{14}H_{11}N_3O$. The yield by this method is extremely small, amounting to only 4 per cent. of that theoretically obtainable according to the equation $C_7H_9N_3O + C_7H_6O + O = C_{14}H_{11}N_3O + 2H_2O$. A much larger yield was obtained on adding an oxidising agent, and the following method was found to give the best results, yielding as much as 60 per cent. of the theoretical.

Phenylsemicarbazide* and benzaldehyde, in molecular proportion, are dissolved in alcohol, and boiled for a few minutes, with the addition of an alcoholic solution of the necessary amount of ferric chloride (2 mol. $FeCl_3$). On adding water, diphenyloxytriazole is precipitated as a mass of brownish needles, which, after being collected and dried, are sufficiently pure for further use. The substance may be purified by crystallising it from boiling alcohol; as the solution cools, the diphenyloxytriazole is deposited as a mass of slender, white needles, which, when rapidly heated, melt at 288°, at the same time undergoing partial decomposition. If more slowly heated, diphenyloxytriazole sublimes in long needles at about 280°. Analysis of the substance recrystallised from alcohol gave results agreeing with the formula $C_{14}H_{11}N_3O$.

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* The phenylsemicarbazide was prepared from phenylhydrazine and potassium

I. 0·1409 gave 0·3656 CO_2 and 0·0599 H_2O.
II. 0·1381 „ 0·3583 „ „ 0·0577 „
III. 0·2124 „ 32·8 c.c. moist nitrogen at 15·5° and 752 mm.

	I.	II.	III.	Calculated for $C_{14}H_{11}N_3O$.
C	70·76	70·75	—	70·88 per cent.
H	4·72	4·60	—	4·64 „
N	—	—	17·85	17·72 „

Specimen I was prepared by the first method, specimens II and III by the second method.

Diphenyloxytriazole is insoluble in cold water, only slightly soluble in boiling water, in cold alcohol, or boiling ether, but easily in boiling alcohol. It has very decided acid properties, its aqueous solution reddens blue litmus paper; it is easily soluble in dilute alkalis, and from the solutions thus obtained it is precipitated unchanged on the addition of hydrochloric acid. It dissolves, on being gently warmed, in a solution of sodium carbonate. The alkaline solution of diphenyloxytriazole has no action on Fehling's solution, even on prolonged boiling.

The silver derivative, $AgC_{14}H_{10}N_3O + H_2O$, is precipitated as a white, amorphous powder on adding silver nitrate solution to a neutral solution of diphenyloxytriazole in aqueous ammonia. The salt, if moist, gradually turns pink on exposure to light, but when washed rapidly with small quantities of alcohol and ether, and dried in a vacuum over sulphuric acid, it is stable. When heated at 110°, the salt gives up its molecule of water.

0·7234 lost, at 110°, 0·0366 H_2O = 5·07.

$AgC_{14}H_{10}N_3O + H_2O$ requires H_2O = 4·97 per cent.

cyanate according to the directions given by Widman (*Ber.*, 1893, **26**, 2613. Footnote). From freshly prepared materials, an almost quantitative yield may be obtained.

0·6675 of the dried salt gave 0·2686 AgCl + 0·0078 Ag. Ag = 31·46

$AgC_{14}H_{10}N_3O$ requires Ag = 31·39 per cent

Diphenyloxytriazole is also a weak base, as it dissolves easily in concentrated hydrochloric acid on warming, and the solution, on cooling, deposits small tufts of needles, which, when dried on a porous plate over caustic potash in a desiccator and analysed, gave figures agreeing with the formula $C_{14}H_{11}N_3O,HCl + 2H_2O$.

0·4672 gave 0·2186 AgCl. HCl = 11·90.

$C_{14}H_{11}N_3O,HCl + 2H_2O$ requires HCl = 11·79 per cent.

The salt gives up the whole of its hydrochloric acid as well as the water of crystallisation when heated at 100°.

0·2949 lost, at 100°, 0·0680. HCl and $2H_2O$ = 23·05

$C_{14}H_{11}N_3O,HCl + 2H_2O$ requires $HCl + 2H_2O$ = 23·39 per cent

The hydrochloride is also easily dissociated by washing with water.

Acetyldiphenyloxytriazole, $C_{14}H_{10}N_3O(C_2H_3O)$.—The acetyl derivative was prepared by boiling the diphenyloxytriazole with acetic anhydride and fused sodium acetate for one hour, using a reflux condenser, dissolving the product in ether, washing several times with potassium carbonate solution, and finally with water. After drying the liquid with calcium chloride, the greater part of the ether was distilled off, and the remainder allowed to evaporate spontaneously, when the acetyl derivative was deposited in well formed prisms, melting at 133°.

0·2158 gave 28·6 c.c. moist nitrogen at 13° and 734·3 mm. N = 15·12.

$C_{14}H_{10}N_3O(C_2H_3O)$ requires N = 15·05 per cent.

Acetyldiphenyloxytriazole is easily soluble in alcohol and ether; on boiling with dilute potassium carbonate solution, it is rapidly hydrolysed to acetic acid and diphenyloxytriazole.

Benzoyldiphenyloxytriazole, $C_{14}H_{10}N_3O(C_7H_5O)$.—The benzoyl derivative, prepared by boiling the oxytriazole with a slight excess of benzoyl chloride, was isolated and purified in precisely the same way as the acetyl derivative. It crystallises in white, flat needles, melting at 134°. It was also prepared from the silver derivative of the oxytriazole by boiling it with an ethereal solution of benzoyl chloride, filtering, and distilling off the ether. It is sparingly soluble in hot water, easily in hot alcohol and in ether. It is easily hydrolysed by warming with potassium carbonate solution.

0·238 gave 25·6 c.c. moist nitrogen at 16° and 759·7 mm. N = 12·53.

$C_{14}H_{10}N_3O(C_7H_5O)$ requires N = 12·31 per cent.

Ethyldiphenyloxytriazole, $C_{14}H_{10}N_3O\cdot C_2H_5$.—This derivative was prepared by heating molecular proportions of diphenyloxytriazole, potassium hydrate, and ethylic iodide (the last in slight excess) with a small quantity of ethylic alcohol in a sealed tube at 100° for one hour; it was also prepared by the action of ethylic iodide at the ordinary temperature on the silver derivative. Both methods gave the same substance. It is easily soluble in alcohol and ether, slightly so in boiling water, and, when recrystallised from dilute alcohol, forms tufts of delicate white needles, which melt at 92°.

Ethyldiphenyloxytriazole is not hydrolysed by boiling with alkalis or acids.

0·1981 gave 27·8 c.c. moist nitrogen at 16° and 761·5 mm. N = 16·38.
0·1924 gave 26·3 c.c. moist nitrogen at 15° and 759·4 mm. N = 16·16.
$C_{16}H_{15}N_3O$ requires N = 15·85 per cent.

Specimen I was prepared with potassium hydroxide, specimen II from the silver salt.

Phenylazocarbamide, $C_6H_5N{:}N{\cdot}CO{\cdot}NH_2$.

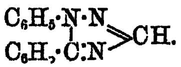
Five grams (1 mol.) of phenylsemicarbazide were suspended in cold water, and a cold aqueous solution of ferric chloride (2 mols. $FeCl_3$) slowly added, the mixture being well stirred. The solution was extracted by agitating with ether so long as the ether became coloured, the process being much shortened if the aqueous solution is saturated with ammonium sulphate. The ethereal solution when distilled on the water bath deposited long, silky, yellowish-red needles, melting at 114°; yield, 4 grams.

0·1519 gave 38·4 c.c. moist nitrogen at 22° and 750·6 mm. N = 28·26.
$C_6H_5N_2{\cdot}CONH_2$ requires N = 28·18 per cent.

Widman (*Ber.*, 1895, **28**, 1925) has quite recently prepared the same substance from nitrosophenylsemicarbazide, and also by the oxidation of phenylsemicarbazide with potassium permanganate in dilute sulphuric acid. I find that the properties of the substance prepared as above agree with those quoted by Widman. I would add that the aqueous solution has a slight but decidedly acid reaction to litmus paper, and that the phenylazocarbamide is slightly volatile with steam. Phenylazocarbamide is slowly formed by the action of moist air on phenylsemicarbazide.

Phenylazocarbamide and benzaldehyde do not react in alcoholic solution at the boiling point, and the addition of ferrous chloride as a condensing agent is without effect; if, however, the alcoholic solution of the two be heated in a sealed tube at 120° for one hour, considerable quantities of diphenyloxytriazole are formed acording to the equation $C_7H_7N_3O + C_7H_6O = C_{14}H_{11}N_3O + H_2O$. The yield is increased in this case by the addition of ferrous chloride.

1 : 5-*Diphenyl*-1 : 2 : 4-*triazole*,



$\begin{array}{l} C_6H_5\cdot N\cdot N \\ C_6H_5\cdot C{:}N \end{array}\!\!>CH.$

This was prepared from the corresponding diphenyloxytriazole by the action of phosphorus pentasulphide according to Andreocci's method (*Real Accad. Lincei*, 1890, ii, 209). Six grams of diphenyloxytriazole were intimately mixed with 10 grams of phosphorus pentasulphide, and the mixture heated for six hours at 230—250°; the dark brown brittle mass thus obtained was boiled with potassium carbonate solution, using a reflux condenser, the solution extracted with ether, and the ethereal solution dried over calcium chloride. On distilling off the ether, a brown oil was left, which rapidly solidified; when recrystallised from water, it formed clusters of fine white needles melting at 91°. Six grams of diphenyloxytriazole yielded 2 grams of the pure product.

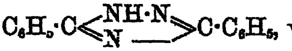
0·2145 gave 36·3 c.c. moist nitrogen at 16° and 742·1 mm N = 19·25.
0·1572 gave 0·4372 CO_2 and 0·0723 H_2O. C = 75·84; H = 5·10.
$C_{14}H_{11}N_3$ requires C = 76·01; H = 4·97; N = 19·00 per cent.

Diphenyltriazole is easily soluble in ether and alcohol, moderately in boiling water, and is sufficiently soluble in cold water to repay extraction of the aqueous mother liquors with ether; it is moderately volatile with steam: as the substance crystallised from the steam distillate in thin, shining plates, it was necessary to ascertain its identity with the substance crystallising in needles, and with this object a nitrogen determination was made and the melting point observed; it melts at 91°.

0·2215 gave 37·1 c.c. moist nitrogen at 12° and 738 mm N = 19·29.
$C_{14}H_{11}N_3$ requires N = 19·00 per cent.

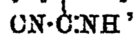
Subsequently the conversion of the one form into the other was noticed during recrystallisation.

Diphenyltriazole sublimes unchanged when heated above its melting point; it is a feeble base; its aqueous solution turns red litmus paper blue, and it forms a hydrochloride and a platinochloride, both of which are dissociated by water. Pinner (*Ber.*, 1894, **27**, 997), by heating benzoylbenzenylhydrazine, prepared an isomeric diphenyltriazole,

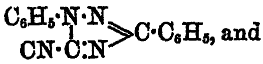


$C_6H_5\cdot C\!\!<\!\begin{array}{l}NH\cdot N\\N\end{array}\!\!>C\cdot C_6H_5$, which he states to have no basic properties.

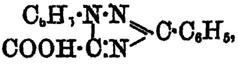
Bladin (*Ber.*, 1889, **22**, 801) by the action of benzaldehyde on phenylhydrazine dicyanide, hydrolysis of the resulting diphenylcyanotriazole, and elimination of carbon dioxide, prepared a diphenyltriazole, to which, considering phenylhydrazine dicyanide to have the constitution



$\begin{array}{l}C_6H_5\cdot N\cdot NH_2\\CN\cdot C{:}NH\end{array}$, and the intermediate products to be

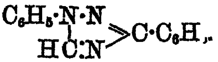


$\left.\begin{array}{l}C_6H_5\cdot N\cdot N\\ CN\cdot C{:}N\end{array}\right>C\cdot C_6H_5$, and

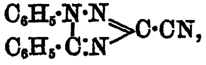


$\left.\begin{array}{l}C_6H_5\cdot N\cdot N\\ COOH\cdot C{:}N\end{array}\right>C\cdot C_6H_5$,

he assigned the constitution



$\left.\begin{array}{l}C_6H_5\cdot N\cdot N\\ HC{:}N\end{array}\right>C\cdot C_6H_5$. It has been shown, however, by Bamberger and de Gruyter (*Ber.*, 1893, **26**, 2385) and by Widman (*Ber.*, 1893, **26**, 2617) that phenylhydrazine dicyanide has the constitution $C_6H_5\cdot NH\cdot N{:}C(CN)\cdot NH_2$, which would give with benzaldehyde,



$\left.\begin{array}{l}C_6H_5\cdot N\cdot N\\ C_6H_5\cdot C{:}N\end{array}\right>C\cdot CN$, and the diphenyltriazole derived from this should be identical with that which I have described above. But the properties quoted by Bladin are entirely at variance with those I have found in my preparation. Bladin describes his substance as a yellow, hard glass, which, on analysis, gave 1½ per cent. too little carbon, but could not be purified as it was not volatile with steam, and separated from the various solvents as an oil. It was, moreover, insoluble in water, soluble with difficulty in ether, and of an extremely feeble basic nature. I have therefore examined Bladin's compound. The diphenyltriazolecarboxylic acid, prepared according to Bladin's directions, was carefully purified, first by fractional precipitation by hydrochloric acid from the solution of its ammonium salt, and then by repeated recrystallisations from alcohol. The properties of the acid agreed with Bladin's description; it crystallised in hard, colourless, flat needles, which melted with effervescence at 176° (Bladin gives 172—182° C.), and lost 1 mol. alcohol of crystallisation at 100°.

0·3222 lost, at 100°, 0·0472. C_2H_6O = 14·65.

$(C_6H_5)_2C_2N_3\cdot COOH,C_2H_6O$ requires C_2H_6O = 14·79 per cent.

0·2132, dried at 100°, gave 29·3 c.c. moist nitrogen at 16° and 756·5 mm. N = 15·94.

$(C_6H_5)_2C_2N_3\cdot COOH$ requires N = 15·84 per cent.

The carefully purified acid was heated in a flask in an oil bath, the temperature of which was slowly raised until the substance began to melt. The temperature was then lowered to 160°, at which it was maintained so long as carbon dioxide was evolved. When cold, the light brown, viscid, syrupy product was treated with ether in the cold, in which the greater part dissolved; the residue was not crystalline. The ethereal solution was filtered and evaporated, and the oily residue extracted with boiling water; the aqueous solution, on cooling, deposited at first a considerable amount of uncrystallisable, tarry matter, and then, after standing for some hours in the cold, a small amount of white, needle-shaped crystals. These melted at 85—87°, and after recrystallisation from dilute alcohol at 90—91°.

The amount of substance thus obtained was too small for analysis, but the melting point, the solubility, and the appearance of the crystals deposited from dilute alcohol, leave no doubt of its identity with the diphenyltriazole prepared from phenylsemicarbazide.

Diphenyltriazole hydrochloride, $C_{14}H_{11}N_3,HCl + 2H_2O$.

Diphenyltriazole dissolves easily in warm concentrated hydrochloric acid; the addition of water to this solution precipitates the diphenyltriazole unchanged if the warm concentrated hydrochloric acid be allowed to cool, the hydrochloride is deposited in bunches of long thin prisms. The salt is easily dissociated by washing with water or by heating to 90°.

0·3241 gave 0·1579 AgCl. HCl = 12·37

0·4623, at 90°, lost 0·1141. HCl and H_2O = 24·68.

$C_{14}H_{11}N_3,HCl+2H_2O$ requires HCl=12·43 and $HCl+2H_2O$=24·69 p c.

Diphenyltriazole Platinochloride, $[C_{14}H_{11}N_3,HCl]_2PtCl_4 + 4H_2O$.

The platinochloride is thrown down as a yellow precipitate on adding platinum chloride solution to a solution of diphenyltriazole in concentrated hydrochloric acid. It is soluble in warm concentrated hydrochloric acid, and crystallises out, on cooling, in long, yellowish-red prisms, containing $4H_2O$, which are given up at 100°.

0·3009 gave 0·0625, Pt. Pt = 20·80.

0·2360, at 100°, lost 0·0191. H_2O = 8·09.

$(C_{14}H_{11}N_3,HCl)_2PtCl_4 + 4H_2O$ requires Pt = 21·15 and H_2O = 7·78 p.c.

Andreocci investigated the behaviour of the platinochlorides of phenyltriazole and phenylmethyltriazole when boiled with water, and when heated at temperatures from 150° to 220° (*Real Accad. Linc.*, 1891, ii, 157). He says that the platinochlorides of the pyrrodiazoles (Andreocci's term for triazoles) resemble in their behaviour the platinochlorides of the pyridine series in that by the action of water, the salts, $R_2H_2PtCl_6$, are converted into compounds of the type R_2PtCl_4, which are yellow powders. The platinochloride of phenylmethyltriazole, when heated to 205°, loses, besides its water of crystallisation, 4 mols. HCl (*loc. cit.*, p. 188); the phenyltriazole salt, on the other hand, loses its water of crystallisation at 100°, 2 mols. HCl when heated at 150—180°, and another 2 mols. HCl at 200—215°, but at this temperature undergoes partial decomposition. Widman, on reinvestigating the platinochloride of the same phenyltriazole, confirmed Andreocci's results. I have studied the behaviour of the platinochloride of diphenyltriazole under the conditions mentioned. When heated to 180°, the salt fused, became somewhat paler in colour, and lost weight. When the weight remained constant, the loss was equal to 4 mols. HCl, plus the water of crystallisation, and an estimation of the platinum in the residue agreed with the formula $(C_{14}H_{10}N_3)_2PtCl_2$.

0·2360 at 180° lost 0·0567. HCl and H_2O = 24·19.

$[C_{14}H_{11}N_3HCl]_2PtCl_4 + 4H_2O$ requires $4HCl + 4H_2O$ = 23·58.

0·2214, heated at 180°, gave 0·0619 Pt. Pt = 27·86.

$[C_{14}H_{10}N_3]_2PtCl_2$ requires Pt = 27·67 per cent.

The behaviour of diphenyltriazole platinochloride when heated to 180° corresponds with that of the platinochloride of phenyltriazole as described in Andreocci's paper.

The behaviour of the platinochloride of diphenyltriazole when treated with water is in agreement with the very feeble basic properties of the substance; when washed with cold water, the red colour slowly disappears, the final residue being a white powder. The same action takes place, only more quickly, when the platinochloride is boiled with water. In both cases platinum tetrachloride and free hydrochloric acid can be detected in the washings, and the white residue is diphenyltriazole, complete dissociation of the salt having taken place.

The reaction by which the diphenyloxytriazole is formed, is being extended to other aldehydes as also to other semicarbazides.

CXII.—*The Vapour Pressures, Specific Volumes and Critical Constants of Normal Hexane.*

By G. L. Thomas, B.Sc., and Sydney Young, D.Sc., F.R.S., University College, Bristol.

A specimen of normal hexane, prepared from propylic iodide by the action of sodium, was obtained from Kahlbaum, and was purified by one of us in December, 1893. It was shaken twice with a mixture of concentrated sulphuric and nitric acids; the first time the acid assumed a deep yellow colour and a good deal of heat was evolved, but the second time there was neither coloration nor rise of temperature. The hexane was then treated three times with a strong solution of potassium hydroxide, washed four times with water, dried with solid potash, and was finally fractionated 11 times from a flask with a long still head, the pure product being collected in two fractions (L and H). The yield of pure hexane was very good.

Specific Gravity.

The sp. gr. of each fraction was determined at two temperatures in a Sprengel tube of the form recommended by Perkin and employed in previous investigations; the weighings were in all cases reduced to a vacuum.

L.		H.	
Temperature.	Sp. gr.	Temperature.	Sp. gr.
0°	0·67696	0°	0·67697
14·95°	0·66384	15·3°	0·66360

Specific Gravities by other Observers.

Name.	Reference.	Sp. gr. at t°.	Calc. at 0°.
Schorlemmer	*Annalen*, 1872, 161, 275	0·6630 at 17°	0·6778
Bruhl	„ 1880, 200, 184	0·6603 „ 20	0·6778
Zander	„ 1882, 214, 165	0·6583 „ 20·9	0·6766
Schiff.......	„ 1883, 220, 87	0·6681 „ 10·8	0·6774
Lachowicz ..	„ „ 220, 192	0·6985 „ 14	0·7113
Perkin......	*Trans. Chem. Soc.*, 1884, 45, 446	0·67392 at 15°/15°	0·68638
„	„ „ „	0·66619 „ 25°/25°	0·68624
Landolt and Jahn	*Zeit. phys. Chem.*, 1892, 10, 290	0·66501 „ 14·2	0·67734
„	„ „	0·66322 „ 16·2	0·67731
„	„ „	0·66141 „ 18·2	0·67728
„	„ „	0 65977 „ 20·1	0·67734

The formula $S_t = 0\ 67696 - 0\cdot0_3854\,t - 0\cdot0_61\,t^2$ agrees very well with our determinations of sp. gr. up to 80°, and has been used in reducing the above observations to 0°.

Boiling Point.

Both fractions were frequently distilled over phosphorus pentoxide and the observed boiling points are given below.*

L.			H.		
Press.	Temp.	Corrected to 760 mm.	Press.	Temp.	Corrected to 760 mm.
mm.	°		mm	°	
734 3	67 8	68·95	731·6	67·7	69·0
737·2	67·9	68·95	720 3	67·25	69·05
751·4	68·55	68·95	737·2	67·9	68·95
749·0	68·55	69·05	760·8	69·05	69·0
760 8	69·05	69·0	747·1	68·5	69·05
758·5	68·95	69·05			
749·7	68·55	69·05			
	Mean...	69·0		Mean...	69·0

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* Two different thermometers were used, about half the observations being made with each.

The value of dp/dt at the boiling point = 22 mm. per degree.

Boiling Points by other Observers.

Name.	Reference.	Boiling point at pressure in mm.	Reduced to 760 mm.
Schorlemmer*	*loc. cit.*	—	71·5°
" †	"	—	69—71
" ‡	*Phil. Trans.*, 1872, 111	—	69—70
Brühl†	*loc. cit.*	68·3—68·4 at 740	69·25
Zander†	"	—	69·0
Schiff§	"	68·6—68·7° at 757·16	68·8
Lachowicz‖	"	—	70·0
Perkin‡	"	—	68—70
Pawlewski¶	*Ber.*, 1883, **16**, 2634	—	68·0
Berthelot**	*Compt. rend.*, 1877, **85**, 831	—	68·5—70
Landolt and Jahn†	*loc. cit.*	—	68·4

Other observations are given in Carnelley's tables of boiling points and melting points.

Note on Specific Gravities and Boiling Points.

The specimens of hexane examined by different observers were obtained from various sources. The specific gravities of the synthetically prepared hexane agree fairly well together, and also with our determinations, but the specimens obtained from petroleum possessed a considerably higher specific gravity.

The observations of the boiling point made by Brühl, Zander, and Schiff agree well with ours, but the others are not very concordant, and in many cases the rise of temperature during distillation seems to have been considerable; this is not to be wondered at in the case of the specimens obtained from petroleum.

Berthelot gives the boiling point of hexane as 69°, though the specimen prepared by him from benzene boiled at 68·5—70°. According to Wreden (*Annalen*, 1877, **187**, 163), hexane cannot be obtained from benzene by the action of hydriodic acid, the final product being hexahydrobenzene, b. p. 69°, sp. gr. 0·76 at 0°.

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* Prepared from hexylic iodide by the action of zinc and hydrochloric acid.

† Prepared from propylic iodide by the action of sodium.

‡ From American petroleum.

§ Prepared from propylic bromide by the action of sodium.

‖ From petroleum from Gallicia.

¶ Source not stated.

** Prepared from benzene by the action of concentrated hydriodic acid under pressure at 270°.

Vapour Pressures at low Temperatures.

The vapour pressures at temperatures below the ordinary boiling point were determined by one of us by the method of Ramsay and Young. For temperatures below 0° with fraction L, a thermometer by Warmbrunn and Quilitz, standardised by the Berlin physikalisch-technische Reichsanstalt, was employed. The effect of alteration of pressure on the zero point was determined and allowed for, and the (very small) correction for the heated column was introduced. The thermometer used for fraction H below 0° was standardised against that of Warmbrunn and Quilitz.

Vapour Pressures below the Boiling Point.

Fraction L.

Press.	Temp.	Press.	Temp.	Press.	Temp.	Press.	Temp.
mm.	°	mm.	°	mm.	°	mm.	°
12·1	−22·18	16·65	−17·35	27·2	−9·21	41·35	−1·75
13·2	−20·80	19·85	−14·55	31·35	−6·77	46·35	+0·43
14·75	−19·25	23·3	−11·88	36·2	−4·06	—	—
43·05	− 0·65	156·75	26·05	418·1	51·25	754·7	68·7
60·85	+ 5·9	206·0	32·4	504·3	56·6	—	—
86·1	12·95	264·5	38·9	591·2	61·5	—	—
116·9	19·4	333·9	45·1	689·7	65·95	—	—

Fraction H.

7·2	−29·7	31·4	− 6·5	147·7	24·9	432·1	52·25
7·7	−28·75	41·45	− 1·5	175·1	28·7	491·1	55·95
9·0	−26·6	52·0	+ 2·65	205·5	32·45	556·4	59·65
10·75	−23·8	64·95	7·25	240·9	36·35	623·0	63·0
13·45	−20·4	80·55	11·4	281·1	40·45	695·3	66·4
17·35	−16 4	101·3	16·25	325·7	44·4	754·8	68·75
23·1	−11·75	122·25	20·4	377·2	48·4	—	—

The vapour pressures at high temperatures were determined with the pressure apparatus employed in previous researches. There were two series of observations, one (I) with a very small quantity of liquid, the other (II) with a larger quantity.

The observed pressures (the mean of four readings in each case), together with those read from the curves constructed from the observations at low temperatures, and also the pressures calculated by means of Biot's formula, are given in the table below. The constants for Biot's formula,

$$\log p = a + b\alpha^t + c\beta^t,$$

are as follows.

$$a = 0{\cdot}504206,$$

$$b = 3{\cdot}207975, \qquad \log b = 0{\cdot}5062310,$$

$$c = -2{\cdot}298881 \qquad \log c = 0{\cdot}3615166,$$

$$\log \alpha = 0{\cdot}00042355,$$

$$\log \beta = \bar{1}{\cdot}99588745,$$

$$t = t^\circ \mathrm{C} + 10.$$

Vapour Pressures.

Temp	Pressures.				Temp.	Pressures.			
	Statical method.		Dynamical from curve.	Calc.		Statical method.		Dynamical from curve.	Calc.
	I.	II.				I.	II		
°	mm.	mm.	mm.	mm.	°	mm.	mm.	mm.	mm.
−30	—	—	6·95	7·45	130·0	3719	3719	—	3723·1
−20	—	—	14·10	14·25	140·0	4606	—	—	4593·0
−10	—	—	25·90	25·90	150·0	5610	—	—	5606 5
0	—	—	45·45	44·92	160·0	6795	6791	—	6777 7
10	—	—	75·00	74·67	170·0	8126	8119	—	8122·9
20	—	—	120·0	119·42	180·0	9650	9651	—	9659·1
30	—	—	185·4	184·40	190·0	11390	11369	—	11407·0
40	—	—	276·7	275·85	200·0	13350	13347	—	13385·0
50	—	—	400·9	400·90	210·0	—	15577	—	15619·0
60	—	—	566·2	567·62	220·0	—	18100	—	18133·0
70	—	—	787·0	784·80	226·0	—	19765	—	19788·0
80	1062	—	—	1062·0	230·0	—	20955	—	20957·0
90	1407	—	—	1409·4	233·0	—	21890	—	21870·0
100	1836	-	—	1837·6	234·0	- -	22220	—	22181·0
110	2358	—	—	2358·0	234·8	—	22510	—	22433 0
120	2982	—	—	2982·1	(critical)				

Volumes of a Gram of Liquid.

The volumes of a gram of liquid were determined with the large quantity of hexane in the pressure apparatus. Up to 150°, the volumes were read directly, but at higher temperatures they were calculated from observations of the volume of vapour and the total volume of liquid and vapour by the method described in the Transactions (1893, **63**, 1200).

The observed and smoothed specific volumes and the molecular volumes calculated from the smoothed specific volumes are given in the following table. In this, as in previous papers, the atomic weights given in F. W. Clarke's *Constants of Nature*, Part V, taking that of hydrogen as unity, are adopted; the molecular weight of hexane is therefore 85·82.

Volumes of a Gram and Molecular Volumes of Liquid.

Temp.	Volumes of a gram.		Mol. vol.	Temp.	Volumes of a gram		Mol vol
	Observed	From curve.			Observed.	From curve.	
0°	1·47719	1·47719	126·77	140·0°	1·8715	1·8715	160·60
10	—	1·4963	128·41	150·0	1·9195	1·9205	164·80
20	—	1·5163	130·13	160·0	1·9755	1·9750	169·30
30	1·5375	1·5374	131·94	170·0	2·0375	2·0355	174·70
40	1·5605	1·5594	133·83	180·0	2·1050	2·1050	180·65
50	1·5830	1·5828	135·84	190·0	2·1885	2·1880	187·80
60	1·6075	1·6075	137·96	200·0	2·2910	2·2910	196·60
70	1·6325	1·6334	140·18	210·0	2·4250	2·4250	208·10
80	1·6605	1·6605	142·54	220·0	2·6250	2·6250	225·30
90	1·6890	1·6897	145·01	226·0	2·8115	2·8115	241·30
100	1·7210	1·7201	147·62	230·0	3·0040	3·0040	257·80
110	1·7530	1·7534	150·48	233·0	3·2890	3·2890	282·25
120	1·7890	1·7894	153·57	234·0	3·4690	3·4690	297·70
130	1·8290	1·8290	156·96	234·8 (critical)	4·2680*	4·2680	366·30

Volumes of a Gram of Saturated Vapour.

The volumes of a gram of saturated vapour were determined by several methods.

1. With the pressure apparatus, from series of readings of the volume of vapour and the total volume of liquid and vapour (*loc. cit.*, compare Amagat, *Compt. rend.*, 1892, **114**, 1093).

2. From the isothermals constructed from the observations of the volumes of unsaturated vapour and of the vapour pressures with the smaller quantity of substance.

3. By the sealed tube method (Trans., 1891, **59**, 37, and *Phil. Mag.*, 1895).

The results are given in the table below, also the volumes of a gram read from a curve constructed by plotting the logarithms of the volumes against the temperatures. The molecular volumes calculated from the smoothed specific volumes are also given.

---

* By the method of Cailletet and Mathais.

Volumes of a Gram and Molecular Volumes of Saturated Vapour.

Temperature.	Volumes of a gram						Molecular volume.
	Pressure apparatus.		Sealed tube method.		Read from isotherms	From curve.	
	I.	II.	I.	II.			
60°	—	—	402·0	—	—	402·0	34500
70	—	—	297·0	—	—	297·0	25500
80	-	—	224·0	—	—	224·0	19200
90	—	—	169·0	—	—	171·0	14700
100	—	—	133·0	—	—	133·0	11400
110	—	—	105·1	—	—	105·0	9010
120	—	—	83·4	—	—	83·3	7150
130	—	—	66·6	—	—	66·6	5720
140	-	—	53·65	53·1	-	53·7	4610
150	42·95		43·55	43·1		43·5	3735
160	35·35	34·85	—	34·8	—	35·3	3030
170	28·95	28·50	—	28·7	28·75	28·8	2470
180	23 72	23·80	—	23 65	23·75	23·65	2030
190	—	19·35	—	19·35	19·35	19·40	1665
200	—	15·90	—	15·75	15·84	15·80	1356
210	—	12·77	—	12·68	12·58	12·66	1086
220	—	9·935	—	9·88	9·81	9·89	849
226	—	8·310	—	—	—	8·31	713
230	--	7·135	—	7·10	-	7·12	611
233	—	6·030	—	6·03		6·03	517
234	—	5·535	—	—	--	5·535	475
{234·8 critical}	—	—	—	—	—	4·268*	306·3*

The critical volumes of a gram and molecular volume were calculated from the critical density which was ascertained by the method of Cailletet and Mathias (*Compt. rend.*, 1886, **102**, 1202; 1887, **104**, 1563; 1892, **115**, 35).

The densities of liquid and saturated vapour, the mean densities and those calculated from the formula

$$D_t = 0·3390 - 0·000446t,$$

are given below.

It will be seen that the agreement between the observed and calculated mean densities is extremely satisfactory.

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* By the method of Cailletet and Mathias.

Mean Densities of Liquid and Saturated Vapour.

Temperature.	Densities.				
	Liquid.	Saturated vapour.	Mean.	Calculated.	$\frac{\Delta}{10000}$.
60°	0·6221	0·0025	0·3123	0·3122	−1
70	0·6122	0·0034	0·3078	0·3078	0
80	0·6021	0·0045	0·3033	0·3033	0
90	0·5918	0·0059	0·2988	0·2989	+1
100	0·5814	0·0075	0·2944	0·2944	0
110	0·5703	0·0095	0·2899	0·2899	0
120	0·5588	0·0120	0·2854	0·2855	+1
130	0·5468	0·0150	0·2809	0·2810	+1
140	0·5343	0·0186	0·2765	0·2766	+1
150	0·5207	0·0230	0·2719	0·2721	+2
160	0·5063	0·0283	0·2673	0·2676	+3
170	0·4913	0·0347	0·2630	0·2632	+2
180	0·4751	0·0423	0·2587	0·2587	0
190	0·4570	0·0515	0·2543	0·2543	0
200	0·4365	0·0633	0·2499	0·2498	−1
210	0·4124	0·0790	0·2457	0·2453	−4
220	0·3810	0·1012	0·2411	0·2409	−2
226	0·3557	0·1203	0·2380	0·2382	+2
230	0·3329	0·1405	0·2367	0·2364	−3
233	0·3040	0·1658	0·2349	0·2351	+2
234	0·2883	0·1807	0·2345	0·2346	+1
{234·8 critical}	—	—	—	0·2343	—

The critical constants are thus found to be as follows.

Density, 0·2343. Volume of a gram, 4·268 c.c.
Molecular volume, 366·3 c.c.
Temperature, 234·8° C.
Pressure, 22510 mm.

It is noteworthy that the critical density is almost identical with that of isopentane, 0·2344.

Volumes of a Gram of Unsaturated Vapour.

Observations of the pressures and volumes of unsaturated vapour were made at a series of temperatures with the smaller quantity of hexane, also a few determinations of pressure and volume at the critical temperature with the larger quantity.

The observations with the unsaturated vapour were made with the object of finding whether the isochors in the case of normal hexane showed any sign ot curvature. Volumes of a gram from about 8 to 35 c.c. were chosen because the curvature of the isochors in the case of isopentane, though always slight, was most pronounced in about this region.

Pressures and Volumes of a Gram at the Critical Temperature

Pressure.	Volume of a gram.	Observations.
mm		
22460	5·320	Tube clear throughout.
22470	5·150	,, ,,
22475	4·979	Faint mist in lower part of tube.
22490	4·807	Mist about half way up, densest at bottom.
22505	4·634	Mist about two-thirds of the way up, densest below, but nearly clear just at bottom.
22500	4·462	Mist densest rather below the middle, clear at top, nearly clear at bottom.
22505	1·290	Mist densest near the middle, clear at top and bottom.
22520	1 119	Mist densest above the middle, clear at top and bottom.
22525	3·918	Mist densest near the top, clear below.
22525	3·778	Mist densest very near the top, clear below.
22530	3 608	Very slight mist at top at first, but soon disappeared.
22585	3·437	Tube clear throughout.
2785	3·266	,, ,,
23250	3 096	,, ,,

Volumes of Unsaturated Vapour.

Temp.	Press.	Volume of a gram.	PV/T.	Temp.	Press.	Volume of a gram.	PV/T.
	mm.	c c.			mm.	c c.	
170°	7058	35·19	560·7	190°	11030	20·49	188·1
	7416	32·94	571·4		11211	19·92	482·4
	7602	31·80	515·6		11377	19·87	475·8
	7804	30·66	540·1	200	7851	35·22	584·6
	7998	29·52	532·9		8172	31·82	570·0
180	7329	35 20	569·5		9229	28·40	551·2
	7698	32·91	559·8		9801	26·13	511·7
	8102	30·66	548·4		10118	23·88	527·6
	8325	29·52	542·6		11151	21·62	509·8
	8556	28·39	530·2		11016	19·37	489·2
	8709	27·26	520·4		12361	18·25	476 9
	9058	26·12	522·3		12801	17·13	463·7
	9327	25·00	514·6		13251	16·01	148·4
	9612	23·87	506·5	210	8069	35·23	588·6
190	7597	35·21	577·8		8759	31·83	577·2
	7967	32·95	567·0		9553	28·41	561·9
	8108	30·67	557·0		10167	26·14	550·2
	8895	28·40	515·7		10852	23·89	536·8
	9131	26·13	532·2		11659	21·62	522·0
	10025	23·88	517·0		12483	19·37	500·7
	10349	22·75	508·5		13441	17·14	476 8
	10682	21·61	408·7		13955	16·01	462·6

Volume of Unsaturated Vapour—continued.

Temp.	Press.	Volume of a gram.	PV/T.	Temp	Press.	Volume of a gram	PV/T.
	mm.	c.c.			mm.	c c.	
210°	14479	14·89	446·4	250°	15894	17·15	521·3
	15028	13·77	428·5		17446	14·91	497·2
	15578	12·65	408·1		18301	13·79	482·4
220	8319	35·24	594·6		19233	12·67	465·8
	9029	31·84	583·1		20248	11 55	447·2
	9876	28·42	569·3		21333	10·43	425·4
	10877	25·02	552·1		22178	9·31	400·1
	12068	21·63	529·5		23675	8·19	370·6
	13006	19·38	511·3	260	9330	35·28	617·5
	14064	17·14	489 0		10168	31·87	608·0
	15241	14·89	460·5		11180	28·45	596·7
	15876	13·78	443·6		12397	25·05	582·6
	16520	12·66	424·1		13892	21·65	564·3
	17173	11·54	402·0		15091	19·40	549·3
	17807	10·42	376·4		16502	17·16	531·2
	18101	9·86	362·0		18161	14·91	508·0
230	8571	35·25	600·6		19119	13·79	494·6
	9311	31·84	589·5		20116	12·67	478·1
	10202	28·43	576·5		21239	11·55	460·4
	11249	25 03	559·7		22470	10 43	439·8
	12521	21·64	538·6		23785	9 31	445·5
	13532	19 38	521·5		25214	8·19	387·4
	14687	17 14	500·6	270	9572	35·29	622 0
	15970	14·90	473·0		10488	31·88	613·4
	16682	13·78	457·0		11500	28·16	602·6
	17425	12·66	438·5		12821	25·05	591·5
	18206	11·54	417·8		14335	21·66	571·7
	19004	10·42	393·8		15604	19·41	557·6
	19761	9·30	365·5		17095	17·16	540 3
	20446	8·18	337·5		18861	14·91	518·0
	20731	7·62	314·1		19869	13·79	504·7
240	8822	35·26	606 3		20997	12·67	490·0
	9599	31·85	596·1		22191	11·56	472·3
	10530	28·43	583·6		23562	10·43	452·8
	11642	25·03	568·1		25072	9·31	430·0
	12989	21 64	547·9		26721	8·19	403·1
	14061	19·39	531·5	280·15	9773	35·29	623·2
	15287	17·15	511·0		10701	31 89	616·5
	16720	14·90	485 7		11791	28·46	606·5
	17506	13·78	470·3		13110	25·06	593·6
	18362	12·66	453·2		14739	21·66	576·8
	19263	11·55	433·6		16087	19·41	561·2
	20191	10·43	410·4		17658	17·17	547·7
	21123	9·31	383·2		19540	14·92	526·7
	22131	8·19	353·1		20638	13·80	514·5
250	9076	35·27	612·0		21847	12·67	500·3
	9888	31·86	602·4		23181	11·56	481·1
	10864	28·44	590·8		24696	10·41	465·7
	12027	25·04	575·9		26377	9 32	441·0
	13449	21·65	557·9		28266	8·19	418·5
	14569	19·40	540·3				

It is customary to map the volumes of a gram of unsaturated vapour against the pressure as in the well-known Andrews' diagram, but in this case the values of PV/T were mapped against v^{-1}. In this way more regular curves are obtained, and the process of smoothing is simplified. The values of PV/T were read at values of

Pressures of Unsaturated Vapour at Definite Volumes.

Volumes of a gram.	9.	12.	15.	18.	21.	24.	27.	30	33 c.c.
Temp.	Pressures in millions.								
170°	—	—	—	—	—	—	—	7915	7104
180	—	—	—	—	—	9573	8859	8233	7686
190	—	—	—	—	10870	9907	9226	8552	7967
200	—	—	—	12156	11366	10408	9583	8869	8219
210	—	—	14139	13063	11852	10815	9027	9164	8507
220	—	16906	15184	13640	12315	11207	10259	9464	8775
230	19975	17882	15918	14230	12798	11611	10614	9767	9045
240	21426	18900	16672	14812	13282	12019	10973	10082	9325
250	22797	19822	17374	15385	13760	12430	11322	10395	9604
260	24163	20787	18101	15953	14226	12828	11667	10696	9870
270	25491	21702	18784	16513	14689	13222	12017	11005	10144
280·45°	26898	22615	19189	17049	15138	13608	12340	11290	10100

Values of dp/dt (= b) at Definite Volumes.

Volumes of a gram.	9.	12.	15.	18.	21.	24.	27.	30.	33.
Temp.	*dp/dt* = *b*.								
170°	—		—	—	—	—	—		—
180	—	—	—		—	—	—	31·8	28·2
190	—	—	—	—	—	42·4	36·7	31·9	28·1
200	—		—	—	40·6	41·1	35·7	31·7	28·2
210	—		—	60·7	48·0	40·7	34·4	29·5	25·8
220	—	—	74·5	57·7	46·3	39·2	33·2	30·0	26·8
230	—	97·6	73·4	59·0	48·3	40·4	35·5	30·3	27·0
240	145·1	101·8	75·4	58·2	48·4	40·8	35·9	31·5	28·0
250	137·1	92·2	70·2	57·3	47·8	41·1	34·9	31·3	27·9
260	136·6	96·5	72·7	56·8	46·6	39·8	34·5	30·1	26·6
270	132·8	91·5	68·3	56·0	46·3	39·4	35·0	30·9	27·4
280	134·6	90·2	67·5	51·3	43·0	36·5	30·9	27·3	24·5
Mean *dp/dt* ...	137·2	95·0	71·7	57·1	47·2	40·1	34·7	30·6	27·1

v^{-1} corresponding to definite volumes, and the pressures were calculated from the data so obtained.

The results are given on the preceding page, also the values of dp/dt (b in the formula of Ramsay and Young, $p = bT - a$). It will be seen that dp/dt is nearly, but not quite, constant at each volume, diminishing slightly with rise of temperature. The deviations from constancy appear to become smaller as the volume increases. In these respects normal hexane resembles isopentane.

The absolute temperatures and the molecular volumes of liquid and saturated vapour were read from the curves at a series of pressures "corresponding" to those given in previous papers; from these data the ratios of the temperatures and volumes to the critical constants were calculated, also the ratios of the actual to the theoretical densities of saturated vapour.

For the sake of comparison, the ratios for isopentane and benzene, the other two hydrocarbons previously investigated, are given in addition to those of normal hexane in the following tables.

Absolute Temperatures, Molecular Volumes, and Ratios of Actual to Theoretical Densities of Saturated Vapour at "Corresponding" Pressures.

Ratios to critical pressures.	Pressures.	Absolute temperatures.	Molecular volumes.		Ratios of actual to theoretical densities of saturated vapour.		
			Liquid.	Saturated vapour.	Norm. hexane.	Isopentane.	Benzene.
	mm.	°					
0·000590	13·30	252·1	—		—	—	
0·001474	33·20	267·25	—	—	—	—	
0·002940	66·40	280·5	127·98	—	—	—	-
0·005898	132·8	295·25	130·51	—	—	—	--
0·011795	265·5	312·0	133·65	—	—	—	—
0·022411	504·5	329·5	137·19	38600·0	1·051	1·040	—
0·044232	995·7	350·75	141·95	20500·0	1·069	1·070	1·052
0·088465	1991·0	376·05	148·47	10650·0	1·103	1·111	1·091
0·14744	3319·0	397·65	155·09	6460·0	1·153	1·159	1·136
0·20642	4647·0	413·6	160·91	4540·0	1·213	1·215	1·180
0·29488	6638·0	431·85	168·90	3105·0	1·302	1·289	1·260
0·44232	9957·0	454·75	181·80	1965·0	1·445	1·427	1·408
0·58978	13280 0	472·65	196·25	1365·0	1·621	1·588	1·582
0·73721	16590·0	487·05	214·3	985·0	1·851	1·825	1·806
0·82568	18590·0	494·6	229·2	813·0	2·034	2·007	2·006
0 88465	19910·0	499·3	242·2	702·0	2·219	2·186	2·180
0·94363	21240·0	503·85	263·1	586·0	2·517	2·488	—
0·97313	21910·0	506·0	282·3	518·0	2·774	2·754	—
1·00000	22510·0	507·8	366·3	366·3	3·827	3·734	3·710

Ratios of Absolute Temperatures and Molecular Volumes to the Critical Constants at "Corresponding" Pressures.

Ratios to critical pressures.	Absolute Temperature. / Absolute critical temperature.			Volume of liquid. / Critical volume.			Volume of saturated vapour. / Critical volume.		
	N. Hexane.	Isopentane.	Benzene.	N. Hexane.	Isopentane.	Benzene.	N. Hexane.	Isopentane.	Benzene.
0·000590	0·4965	—	0·4795	—	—	0·3359	—	—	—
0·001474	0·5263	—	0·5098	—	—	0·3428	—	—	—
0·002949	0·5524	0·5366	0·5359	0·3494	—	0·3489	—	—	—
0·005898	0·5814	0·5660	0·5645	0·3564	—	0·3560	—	—	—
0·011795	0·6144	0·5994	0·5989	0·3649	0·3685	0·3648	—	—	—
0·022411	0·6489	0·6346	0·6334	0·3746	0·3780	0·3742	105·4	101·6	—
0·044232	0·6907	0·6777	0·6765	0·3876	0·3910	0·3870	55·9	53·5	54·4
0·088465	0·7406	0·7282	0·7292	0·4053	0·4036	0·4053	29·1	27·7	28·2
0·14744	0·7881	0·7782	0·7725	0·4234	0·4263	0·4233	17·6	16·9	17·25
0·20642	0·8145	0·8059	0·8052	0·4393	0·4421	0·4389	12·4	12·0	12 85
0·29488	0·8504	0·8434	0·8429	0·4611	0·4636	0·4602	8·48	8·29	8·49
0·44232	0·8955	0·8902	0·8906	0·4964	0·4959	0·4960	5·36	5·27	5·35
0·58978	0·9308	0·9266	0·9270	0·5357	0·5388	0·5353	3·73	3 69	3·72
0·73721	0·9591	0·9566	0·9566	0·5851	0·5884	0·5845	2·69	2·65	2·69
0·82568	0·9740	0·9722	0·9725	0·6258	0·6275	0·6250	2·22	2·19	2·20
0·88465	0·9833	0·9800	0·9824	0·6612	0·6656	0·6613	1·92	1·89	1·91
0·94363	0·9922	0·9918	0·9915	0·7184	0·7232	0·7113	1·60	1·58	—
0·97318	0·9965	0·9963	—	0·7706	0·7755	—	1·41	1·39	—
1·00000	1·0000	1·0000	1 0000	1·0000	1·0000	1·0000	1·00	1·00	1·00

It will be seen that there is a very fair agreement between the ratios for the three hydrocarbons.

The ratios of the absolute temperatures to the absolute critical temperatures are somewhat higher for normal hexane than for either isopentane or benzene. With regard to the comparison with isopentane, it may be pointed out that, in the case of the ethereal salts, the ratios increase with rise of molecular weight in any homologous series, also that in the comparison of methylic butyrate and methylic isobutyrate, the ratios for the iso-compound are slightly lower than for the normal salt. It seems not unlikely that the paraffins may be found to resemble the ethereal salts, at any rate as regards the influence of molecular weight.

The agreement with benzene in the case of the molecular volumes of liquid and saturated vapour is extremely close, and with isopentane it is fairly so. Here again it may be pointed out that no connection could be traced between the volume ratios for the ethereal salts and the molecular weights, though in the case of isomeric ethereal salts the ratios appeared to depend to some extent on the chemical constitution. Thus, the ratios of the volumes of liquid to the critical volume are higher for methylic isobutyrate (the only iso-compound investigated) than for any of the nine normal salts, whilst for the saturated vapour the ratios are lower than for any of the others. So also with the two paraffins, the ratios of the volumes of liquid to the critical volume are higher for isopentane than for normal hexane, and for the saturated vapour they are lower. It is hoped that an investigation of the thermal constants of other paraffins may throw further light on these points.

CXIII.—*Some Constituents of the Root of* Polygonum cuspidatum.

By A. G. PERKIN, F.R.S.E.

AMONG the different varieties of the species Polygonum, that best known is perhaps the *P. tinctorium*, the leaves of which are used as a source of indigo in China, Japan, and some parts of Russia. Of others, the *P. aviculare* and *barbatum* yield a blue colour, probably indigo, and the *P. hydropiper* and *tortosum* are said to contain a yellow colouring matter; moreover, the roots of some of these varieties possess medicinal value.

The *P. cuspidatum*, which is common in parts of India, China, and Japan, has evidently attracted but little attention, the only reference found bearing on its properties being the following, contained in a paper (*Journal Royal China Branch of Royal Asiatic Society*, **22**, New Series, No. 5, 1887), by A. Henry, M.A., L.R.C.P., entitled "Chinese Names of Plants," "*Kan-yen, wu-tzu*, name at Patung for the root of *P. cuspidatum*, which is said to be used for dyeing yellow."

During the removal of some of this plant from my garden, my attention was directed to the root on account of its strong colour internally and its somewhat close resemblance to madder and morinda root. As much as could be obtained was therefore collected for examination, and for a further quantity I am indebted to Mr. Richard Reynolds, F.I.C., of Leeds, by whom the plant was originally introduced into this district. The roots vary in diameter from ¼ in. to 1 in. when fresh, and consist of a thick succulent bark, internally of an orange-red colour, and a central light yellow, woody portion; the former, on drying, shrivels considerably and becomes lighter in tint. As examination showed that the woody portion contained but little extractive matter, the bark only was preserved, and of this in the dry condition 600 grams was obtained.

EXPERIMENTAL PART.

The Glucoside Polygonin.

The ground root bark was extracted twice with 10 times its weight of boiling alcohol for six hours, and the resulting orange-brown extracts evaporated to a small bulk. The residual liquid, from which nothing separated out on standing, was treated with water and extracted with ether, the ethereal solution being placed aside for subsequent examination. The addition of baryta water to the aqueous liquid produced a dirty white precipitate, which was removed by filtration, and washed with water until the washings were nearly colourless. The deep red filtrate, after being neutralised with acetic acid and saturated with common salt, was extracted with a large volume of ethylic acetate, and the extract evaporated; as the solution became concentrated, a brown gelatinous precipitate commenced to separate, and a further quantity was deposited on cooling. This product, which appeared under the microscope as a mixture of gelatinous and crystalline matter, was collected, rinsed with ethylic acetate, pressed, and dissolved in boiling alcohol, it being necessary, however, to previously grind the mass into a thin cream with the solvent, otherwise complete solution could only be obtained by protracted digestion. On evaporating to a small bulk and cooling, the liquid deposited a gelatinous matter; directly this ceased to form, it was rapidly filtered, and the crystalline substance which separated from the filtrate was collected and purified by crystallisation from acetic acid. The gelatinous portion, when dissolved in boiling alcohol and treated in the manner above described, yielded more of the crystalline matter, the operation being repeated until at length crystals could no longer be obtained from the gelatinous matter which separated; the latter was then placed aside for subsequent examination. Analyses of distinct preparations of the crystalline substance gave the following numbers.

0·1151 gave 0·2460 CO_2 and 0·0510 H_2O. C = 58·28; H = 4·92.
0·1091 „ 0·2340 „ „ 0·0495 „ C = 58·48; H = 5·04.
0·1095 „ 0·2325 „ „ 0·0495 „ C = 57·90; H = 5·02.
$C_{21}H_{20}O_{10}$ requires C = 58·33; H = 4·63 per cent.

It consisted of a glistening mass of orange-yellow needles, which, when heated, softened at 200° and melted at 202—203°. From its solution in boiling alcohol, in which it is but sparingly soluble, it is deposited in a gelatinous condition if rapidly cooled, but when left to cool slowly it separates as a bulky mass of hair-like needles. Boiling water and ethylic acetate dissolve it sparingly, and it is almost insoluble in ether. With cold dilute alkalis or baryta water, it yields orange-red liquids, and by treating a boiling alcoholic solution of the substance with alcoholic potash, the potassium derivative separates, on cooling, in the form of red, flat, microscopic needles. The lead salt, an orange-red amorphous powder somewhat soluble in boiling water, is formed when lead acetate is added to an alcoholic solution of the substance.

Emodin.

Experiment soon revealed the fact that the above-described substance was a glucoside, and, in order to determine its nature, its solution in 60 per cent. alcohol was digested at the boiling heat with a small quantity of hydrochloric acid. During this operation, the light yellow liquid quickly became orange-red, and crystals separated; when the action had ended, boiling water was added a little at a time, and the mixture allowed to cool. The product was collected, washed with water, and dried at 120°.

0·1224 gave 0·2980 CO_2 and 0·0450 H_2O. C = 66·39; H = 4·08.
$C_{15}H_{10}O_5$ requires C = 66·66; H = 3·70 per cent.

Thus obtained, it formed orange-red needles readily soluble in alcohol; it melted at 253—254°, and sublimed at higher temperatures with partial carbonisation. When distilled with zinc dust, a sublimate of greenish leaflets was produced, which, after crystallisation from alcohol, melted at 203°, and appeared to be identical with α-methylanthracene. Dilute alkalis and ammonia dissolved it with a red coloration, but it was almost insoluble in baryta water. The alkaline solutions when boiled with zinc dust became yellow, but on exposure to air regained their original tint. When it was dissolved in nitric acid (sp. gr. 1·54) and the solution evaporated to a small bulk and cooled, a semi-solid mass was obtained which crystallised from acetic acid in long, thin, orange-yellow needles. This product dissolved in solutions of the alkali hydroxides with a red coloration, decomposed with a slight explosion when strongly heated, and evidently consisted of a nitro-derivative. To convert the substance $C_{15}H_{10}O_5$ into its acetyl compound, it was digested at the boiling temperature with a small quantity of acetic anhydride for three hours. On cooling, crystals separated, which, after recrystallisation from alcohol, formed lemon-yellow needles melting at 189°. Sufficient was not available for analysis. These results showed that the substance $C_{15}H_{10}O_5$ is *emodin*, a trihydroxy-α-methylanthraquinone, existing in rhubarb root (De la Rue and Muller, *J. Chem. Soc.*, 1857, **10**, 298), and also in the bark of *Rhamnus frangula*, as a glucoside (Trans., 1892, **61**, 1, Thorpe and Miller). The acetyl-emodin melts at 190° (Liebermann, *Ann.*, 1876, **183**, 161), and it has been previously shown (Trans., 1894, **65**, 934) that emodin reacts with nitric acid to form a nitro-derivative.

A determination of the amount of emodin produced by the hydrolysis of the glucoside gave the following result.

0·3858 glucoside yielded 0·2385 emodin, or 61·82 per cent.

This result is in accordance with the following equation :—

$$C_{21}H_{20}O_{10} + H_2O = C_{15}H_{10}O_5 + C_6H_{12}O_6,$$

which requires 62·50 per cent. of emodin.

The filtrate from the emodin, after neutralisation with silver carbonate and evaporation, yielded an almost colourless syrup, but obviously in too small a quantity for purification. A solution of the substance reacted with phenylhydrazine acetate, on gently warming; lemon-yellow aggregates of an osazone being deposited on cooling. The examination of this glucose must be deferred until more raw material is forthcoming.

Frangulin, the only glucoside of emodin hitherto known, and found in *Rhamnus frangula*, is not identical with the above. When hydrolysed, for instance, it yields emodin and rhamnose (Thorpe and Miller, *loc. cit.*),

$$C_{21}H_{20}O_9 + H_2O = C_{15}H_{10}O_5 + C_6H_{12}O_5,$$

a reaction which requires 64·9 per cent. of emodin, and its difference in composition ($C_{21}H_{20}O_9$ requires C = 60·57; H = 4·80), crystalline appearance, solubility, and other properties from the glucoside found in *Polygonum cuspidatum*, show clearly that they are distinct substances. I propose to give the name *polygonin* to this new glucoside of emodin from the *Polygonum cuspidatum*.

Emodin Monomethyl Ether.

The gelatinous residue obtained during the purification of the polygonin, had the properties of a glucoside, but as the quantity obtained did not exceed 0·1 gram, it could not be examined in this condition, but was at once hydrolysed by digestion with dilute hydrochloric acid, when a dirty, orange-coloured crystalline product was obtained; this, by crystallisation from alcohol was separated into emodin, which is readily soluble, and a second substance, characterised by its sparing solubility in this liquid. By recrystallisation, the latter was obtained in yellow needles melting at 199°, though from more dilute solutions it was deposited in leaflets. It differs from emodin, also, in that it is insoluble in dilute ammonia, and almost so in alkalis of moderate strength. Its solution in sulphuric acid is also slightly bluer than the corresponding solution of emodin. While examining this substance, I was struck not only by the nearness of its melting point to that of emodin methyl ether (m. p. 200°) found in the root bark of the *Ventilago madraspatana* (Perkin and Hummel, Trans., 1894, **65**, 932), but also by the similarity of their appearance and properties. The quantity of substance available for experiment was only 0·05 gram, and, as the question of its identity could not be decided by analysis only, it was thought better to test its behaviour with sulphuric acid at 160°; for, in case it were the emodin methyl ether, it would thus yield emodin. The product of the action of sulphuric acid was accordingly treated with water, and the dirty, orange-coloured precipitate thus produced was collected and purified, first by crystallisation from dilute alcohol, and, finally, from toluene. The orange-coloured needles thus obtained melted at 253—254°, dissolved readily in ammonia, and, without doubt, consisted of emodin. It therefore follows that the substance melting at 199°, obtained from *Polygonum cuspidatum*, is identical with the emodin monomethyl ether which exists in *Ventilago madraspatana*. In the former it is present in the condition of glucoside, but, as previously shown (*loc. cit.*), it exists in the latter root in the free state.

It is interesting to note that Schwabe (*Arch. Pharm.*, 1888, **26**, 569), and subsequently Thorpe and Miller (Trans., 1892, **61**, 6), isolated from the bark of *Rhamnus frangula* not only frangulin, but a second substance, to which they respectively assigned the melting points 199°, and 202—203°, and this was considered by the latter authors to be probably a trihydroxymethylanthraquinone isomeric with emodin. The properties of this substance agree very closely with those of the emodin methyl ether above described, and it appears possible that they may be identical. Experiments will be instituted with *Rhamnus frangula* to decide this point.

The Wax.

The ethereal extract, obtained during the isolation of the glucoside, was extracted with dilute alkali, the red-coloured extract neutralised with acid, and the orange-red flocks thus formed were collected and purified by crystallisation from toluene; the product consisted of orange-coloured needles melting at 253—254°, and had all the properties of emodin. The quantity of emodin obtained from the root in the free state was exceedingly small.

As the remaining ethereal solution appeared to contain a wax, it was evaporated to dryness, and the colourless, sticky residue dissolved in a small quantity of boiling alcohol. On standing, the solution deposited warty nodules, and these were collected and purified by further crystallisation. The product consisted of beautiful, colourless leaflets which resembled phenanthrene in appearance, and melted at 134—135°. In melting point* and properties it appeared identical with the wax existing in the root bark of the *Morinda umbellata* (Perkin and Hummel, Trans., 1894, **65**, 867), and, though the quantity obtained was very small (0·06 gram), it appeared evident that, if the two were identical, an analysis would yield numbers agreeing approximately with those formerly given (*loc. cit.*). This proved to be the case.

0·0536 gave 0·1635 CO_2 and 0·0560 H_2O. C = 83·19; H = 11·60.
$C_{18}H_{28}O$ requires C = 83·08; H = 10·75 per cent.

The wax contained in the root of the *Polygonum cuspidatum* is, therefore, identical with that existing in the root of *Morinda umbellata.*

The chief constituents of the root of *Polygonum cuspidatum* are thus shown to be a glucoside polygonin, $C_{21}H_{20}O_{10}$, which yields emodin on hydrolysis, also free emodin, an emodin monomethyl ether, and a wax, $C_{18}H_{28}O$. In containing emodin, it shows a chemical connection with the rhubarb root, and with the bark of *Rhamnus frangula* in containing emodin methyl ether; also a connection with *Ventilago madraspatana* root, and a similar relationship with the *Morinda umbellata*, in that they both contain identical waxes.

Dyeing experiments with the root, using mordanted calico, showed, as was to be expected from the chemical examination, that it was devoid of useful tinctorial properties; faint, dull shades were obtained, evidently due to the presence of a small quantity of tannin matter. It is thus evident that no yellow colouring matter is present in this portion of the plant. Examination, however, showed that the *leaves* contain a small quantity of a substance which yields yellow shades with alumina mordant, and it is possible that some confusion has arisen between the leaves and the root with regard to this property.

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* The melting point of this wax given in the former paper is 124—125°, an error which appears to have arisen during the correction of the proof sheets.

It is my intention to study the constituents of the roots of the *Polygonum bistorta* and *Rumex nepalensis*—members of two closely-allied species.

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CXIV.—*A New Series of Hydrazines.*

By Frederick D. Chattaway, B.A., and Harry Ingle, B.Sc.

Since the discovery of the primary and secondary hydrazines, they have become of such importance as synthetic agents, and the results to which their employment has led have been of such magnitude that other substituted derivatives of hydrazine have been but little studied.

Theoretically, hydrazine can yield five series of substituted derivatives, the primary, secondary, symmetrical and unsymmetrical, tertiary, and the quaternary.

$H_2N{\cdot}NH_2$;	Hydrazine.
$RHN{\cdot}NH_2$;	Primary.
$RHN{\cdot}NHR$;	Secondary symmetrical.
$R_2N{\cdot}NH_2$;	Secondary unsymmetrical.
$R_2N{\cdot}NHR$;	Tertiary.
$R_2N{\cdot}NR_2$;	Quaternary.

Actually only three of these series are known, the primary, the secondary symmetrical, usually known as the hydrazo-compounds, and the secondary unsymmetrical. No simple method of obtaining members of the other series has hitherto been described, and in spite of many efforts, only isolated mixed derivatives have been produced.

The present paper is the introduction to an investigation of the tertiary and quaternary hydrazines which the authors have undertaken, these bodies being of great interest, not only as a new series of well-defined compounds, but also on account of their probable bearing on the theory of the stereo-isomerism of nitrogen. The quaternary hydrazines alone will be dealt with in this paper.

These compounds can be obtained from the secondary amines by a simple general reaction, which renders it possible to prepare any tetra-derivative of hydrazine containing either similar or dissimilar radicles, the constitution of the compound following with certainty from its mode of formation.

The secondary amine is treated with sodium or sodium ethoxide, whereby the hydrogen atom is displaced by sodium.

$$2R_2NH + 2Na = 2R_2NNa + H_2.$$

The equivalent quantity of iodine is then allowed to act on this sodium compound when the sodium atoms are withdrawn, and the two amine residues unite to form the quaternary hydrazine.

$$2R_2NNa + I_2 = R_2N{\cdot}NR_2 + 2NaI.$$

The compounds which have so far been carefully examined are those containing simple aromatic residues. They are solid, stable substances, easily obtained in large, measurable crystals, and behaving exactly as would be expected from their constitution. They are not easily oxidised, and scarcely, if at all, basic, but appear to yield double hydrazonium compounds, and bases analogous to those formed from the tertiary amines. The percentage composition of these hydrazines and their molecular weights, determined by Raoult's method, agree well with the theoretical, and the yields are very good, being in some cases nearly quantitative.

Tetraphenylhydrazine, $(C_6H_5)_2N{\cdot}N(C_6H_5)_2$.

In the preparation of this compound, diphenylamine (melting point 54°) is dissolved in about 10 times its weight of dry ether, and twice the theoretical amount of sodium ethoxide, shaken up with ether or dissolved in the least possible quantity of alcohol, is added; the clear solution of the amine becomes turbid, and a white, bulky precipitate of the sodium compound is thrown down.

$$(C_6H_5)_2NH + C_2H_5{\cdot}ONa = (C_6H_5)_2NNa + C_2H_5{\cdot}OH.$$

To this is added, after a lapse of 12 hours, a quantity of iodine, dissolved in ether, and equivalent to the amount of sodium used; sodium iodide is precipitated, the hydrazine remaining dissolved in the ether.

$$2(C_6H_5)_2NNa + I_2 = 2NaI + (C_6H_5)_2N{\cdot}N(C_6H_5)_2.$$

After having been left for a few hours, the ethereal solution is poured off, washed with water and very dilute sodium carbonate solution, and dried over fused calcium chloride. On distilling off the bulk of the ether, and, if necessary, adding a little hot alcohol, the hydrazine separates as a brownish, crystalline powder. It may be purified by repeated recrystallisation from chloroform and alcohol. As the hydrazine is very easily soluble in chloroform, the operation is best carried out as follows. The compound having been dissolved in a small quantity of warm chloroform, about five times its bulk of hot alcohol is added to the solution, and the whole allowed to cool gradually; the hydrazine then crystallises out in long orthorhombic prisms of a faint brown or flesh colour. The slight coloration is apparently due to some very small admixture of impurity, which cannot be got rid of by recrystallisation, but varies somewhat with the nature of the solvent.

Tetraphenylhydrazine is easily soluble in benzene, chloroform, and acetone, slightly soluble in hot alcohol, and insoluble in water. It melts at 147°, with slight decomposition. It dissolves in hot, glacial acetic acid, giving a violet solution, from which no salt crystallises out, and the compound, on dilution, seems to be reprecipitated in an impure form. It dissolves easily in cold, concentrated, sulphuric acid, giving a deep purple solution, which, on exposure to the air, or on heating, changes to a deep indigo blue. Fehling's solution, boiled with the finely powdered hydrazine, shows no sign of reduction.

The results of the analyses agree well with the formula, as does also the molecular weight found.

0·3082 gave 0·9702 CO_2, and 0·1641 H_2O. C = 85·85; H = 5·93.
0·3680 „ 26·4 c.c. moist nitrogen at 20°, and 768·5 mm. N = 8·29.
$(C_6H_5)_4N_2$ requires C = 85·71; H = 5·95; N = 8·33 per cent.

The molecular weight was determined by Raoult's method, using benzene as a solvent.

0·6718 gram of the substance dissolved in 21·9 grams of benzene, lowered the freezing point by 0·46°.
0·6718 gram of the substance dissolved in 33·9 grams of benzene, lowered the freezing point by 0·3°.

These give the molecular weight as 327 and 324 respectively, whilst the formula $(C_6H_5)_4N_2$ requires 336.

Measurements of Crystals.

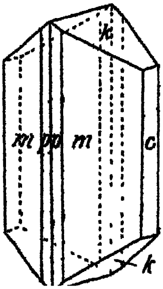
Dr. Lapworth, who very kindly undertook the examination of the crystals, has communicated to us the following details.

Crystalline System: Orthorhombic.
a : *b* : *c* = 0·6301 : 1 : 0·9325.

FIG. 1.

Forms observed:

c	{001}
k	{101}
m	{011}
p	{031}



The following angular measurements were obtained.

Angle.	No. of observations.	Limits.	Mean.	Calculated.
mk = 011 : 101	24	111° 1′—111° 18′	111° 11′	—
mc = 011 : 001	20	42 50 — 43 10	43 0	—
ck = 001 : 101	14	55 14 - 56 5	55 55	55° 56′
kk = 101 : $10\bar{1}$	11	67 58 — 68 20	68 10	68 8
mm = 011 : $01\bar{1}$	10	93 50 — 94 1	93 58	94 0
mp = 011 · 031	14	27 14 — 27 25	27 20	27 20
pp = 031 : $03\bar{1}$	6	39 15 — 39 36	39 25	39 20
kp = 101 : 031	6	79 1 — 79 24	79 10	79 8
mm = 011 : $0\bar{1}1$	20	85 46 — 85 15	86 0	86 0

Tetraphenylhydrazine crystallises in prisms, the faces of which, as a rule, give excellent images. The predominant forms are *m*{011} and *k*{101}, the forms *c*{001} and *p*{031} are usually also present, but less developed.

The acute optic axial bisectrix emerges through *c*{001}, the axial plane is *a*{100}. The axial angle is very small, so that a hasty examination of the interference figure, with a 1/10 in. immersion objective gives the impression that the crystal is uniaxial. The double refraction is strong and negative, and the dispersion is fairly strong. The crystals show no obvious cleavage.

Tetraparatolylhydrazine, $(C_6H_4{\cdot}CH_3)_2N{\cdot}N(C_6H_4{\cdot}CH_3)_2$.

In the preparation of this substance, paraditolylamine (melting point 79°) is dissolved in 10 times its weight of dry ether, twice the theoretical amount of sodium ethoxide suspended in ether is added, and the mixture left for about 12 hours. A quantity of iodine equivalent to the sodium used is added, and after a few hours the ethereal solution of the hydrazine is treated as in the preparation of the phenyl compound. On distilling off most of the ether, and allowing the residue to cool slowly, the tetraparatolylhydrazine crystallises out in nearly theoretical amount; it may be purified by recrystallisation from a mixture of chloroform and alcohol, and finally from acetone; from the latter solvent it separates in very fine, monoclinic tablets. The crystals are soft and brittle, very much like resin in behaviour, and of a pale-yellow colour. It melts at 138°, decomposing slightly, the melting point appearing to vary somewhat with the rapidity of heating. It is very readily soluble in benzene, chloroform and acetone, slightly in hot alcohol, and insoluble in water. Cold, concentrated sulphuric acid readily dissolves the hydrazine, giving a brilliant azure blue solution, which only slowly alters on exposure to air. The addition of a little nitric acid changes this to green, and finally to brown. No reduction takes place when the finely powdered hydrazine is boiled with Fehling's solution.

The numbers obtained for its composition and molecular weight agree closely with the theoretical ones, whilst the constitution is established by its mode of formation

0·2155 gave 0·6651 CO_2 and 0·1344 H_2O. C = 85·76; H = 7·07.
0 3317 „ 21·6 c.c. moist nitrogen at 20° and 750·6 mm. N = 7·34.
$(C_6H_4{\cdot}CH_3)_4N_2$ requires C = 85·71; H = 7·14: N = 7·14 per cent.

The molecular weight was determined by Raoult's method, using benzene as a solvent.

0·5212 gram of the hydrazine dissolved in 23·96 grams of benzene, lowered the freezing point by 0·265°.

This gives 402 as the molecular weight, whilst the formula $(C_6H_4{\cdot}CH_3)_4N_2$ requires 392.

Measurements of Crystals.

Dr. Lapworth has furnished us with the following description of the crystals.

Crystalline system: Monoclinic.

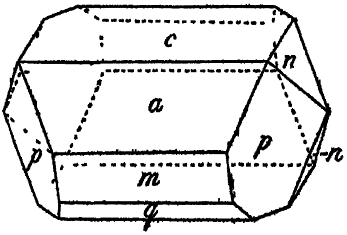
$a : b : c = 2{\cdot}3217 : 1 : 2{\cdot}6330.$

$\beta = 59° 45'.$

Forms observed:

a	{100}
c	{001}
m	{101}
q	{102}
p	{111}
n	{011}

FIG. 2.



Angle.	No. of observations.	Limits.	Mean.	Calculated.
cn = 001 : 011	16	66° 5′—66° 55′	66° 16′	—
an = 100 : $01\bar{1}$	16	78 11—78 31	78 18	-
cm = 001 : 101	8	66 14—66 36	66 22	—
nn = 011 : $01\bar{1}$	8	47 13—47 40	47 28	47° 28′
ac = 100 : $00\bar{1}$	6	59 41—59 46	59 43	59 45
am = 100 : 101	6	53 22—53 57	53 40	53 53
mq = 101 : 102	3	31 50—32 5	31 59	31 56
cq = 001 : 102	3	34 15—34 31	34 20	34 26
np = $01\bar{1}$: 111	2	40 25—40 34	40 29	40 32
np = 011 : 111	6	26 8—26 24	26 13	26 13
ap = 100 : 111	6	74 58—75 39	75 24	75 29
nq = 011 : 102	4	69 3—71 3	70 22	70 37
mn = 101 : 011	2	80 31—80 39	80 35	80 42

Angle.	No of observations.	Limits.	Mean.	Calculated.
pq = 100 : 102	3	68 50—69 13	69 3	68 51
mn = 101 : $01\bar{1}$	6	99 12—99 35	99 25	99 18
cp = 001 : $\bar{1}11$	4	99 30—99 59	99 41	99 49
pm = 111 : 101	4	61 40—61 51	61 44	61 49
pp = 111 . $\bar{1}1\bar{1}$	2	50 12—50 24	50 18	50 21

Tetraparatolylhydrazine crystallises in monoclinic prisms or plates of considerable size; they are of a faint yellow colour, and appear readily to undergo a process of re-solution, as the faces are invariably somewhat convex; in spite of this, however, they give very definite images, so that concordant measurements can be obtained.

The crystals are usually prismatic, having the appearance shown in Fig. 2, but some are plate-like, the form *a*{100} being enormously developed.

The forms *n*{011} and *q*{102} are usually absent from the plates, the forms *a*{100}, *a*{001}, and *p*{111} predominating, both in the prisms and the plates.

The optic axial plane is the plane of symmetry, the acute bisectrix emerging through *a*{100}. The axial angle is large; the double refraction is negative and strong; the dispersion is weak. The crystals show an imperfect cleavage parallel to *a*.

The authors are continuing this investigation, and later hope to communicate the results to the Society.

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CXV.—*Sodium Nitrososulphate.*

By Edward Divers, M.D., F.R.S., and Tamemasa Haga, D.Sc., F.C.S.

Pelouze (*Ann. Chim. Phys.*, 1835, [2], 60, 151; *Annalen*, 1835, 15, 240), in attempting to prepare sodium nitrososulphate, found it to be far more soluble than potassium or ammonium nitrososulphate, and therefore difficult to prepare. As its general properties in solution seemed to be the same as those of the potassium salt, he did not proceed to isolate it or to examine it further.

The potassium and ammonium salts crystallise out when a fairly concentrated solution of the respective sulphite, along with some excess of alkali, is submitted to the action of nitric oxide, but this is not the case with the sodium salt, which can only be obtained by evaporating the solution left after acting on sodium sulphite with nitric oxide. We prepared it by exposing for five days, at about the mean temperature, to an atmosphere of nitric oxide, a very concentrated solution of normal sodium sulphite, to which, as a preservative, one-fortieth of its weight of sodium hydroxide had been added; it was contained in a connected series of Erlenmeyer flasks, the layer of liquid being shallow. For half this time, the gas was under the additional pressure of a column of water, and for the rest of the time at the barometric pressure only. The flasks were occasionally shaken, but as no incrustation was formed on the surface of the solution, agitation was less useful than in making the potassium or ammonium salt.

At the end of five days, the solution was effervescing slightly, indicating that the salt was undergoing decomposition. Hardly any sulphite then remained, and nearly all the sulphate which had formed or been present at starting was crystallised out by keeping the solution for some time at a little below zero; this was removed, and the solution quickly evaporated in a vacuum desiccator to a very small volume, by which time it had deposited opaque white crusts and minute hard crystals, perfectly transparent under the microscope. These, which proved to be nitrososulphate, were placed on a porous tile and drained dry; the salt then formed a crystalline powder, tasting remarkably like common salt, slightly alkaline to litmus, and free from sulphate and sulphite. It was weighed and then left for a night in a desiccator, to see what it would lose in weight as moisture and water of crystallisation; next morning it appeared to be unchanged, and was placed on the balance-pan between watch-glasses, but it could not be weighed because it rapidly lost weight. Taken from the balance and uncovered, it had not been a minute exposed to the air before it began to have a nitrous odour, and then quickly grew very hot and evolved much nitrous oxide mixed with nitric oxide. The watch-glass which held the salt was broken, and the wood of the table on which it rested was scorched by the heat. The powdery solid residue of the decomposed salt, consisting of sulphate and sulphite, was collected, with hardly any noticeable loss, and weighed. Its weight was 5·645 grams, while the nitrososulphate as placed in the desiccator had weighed 7·595 grams. In portions of the residue we determined its sodium by ignition with sulphuric acid, its sulphur by oxidation with bromine water and precipitation with barium chloride, and its sulphite by titration with iodine. These were all calculated as parts per cent. of the salt before it was placed in the desiccator. The numbers found show a deficiency of about 3 per cent. from those for the anhydrous salt, whilst sodium nitrososulphate with $1H_2O$ would have lost 8·8 per cent. in becoming anhydrous. The tabulated numbers are given.

	$Na_2N_2SO_5$.	Found.	$Na_2N_2SO_5$ with 3 p. c deficient.
Sodium	24·73	24·13	23·99
Sulphur	17·20	16·64	16·68

This deficiency includes moisture, and any solid particles carried away during the very rapid evolution of gas by the salt when decomposing. From the weight of the residue and that of the sulphite it contained, it can be calculated, approximately at least, that about 1·6 per cent. of the original salt, or 1·2 per cent. of sulphate and sulphite, were mechanically lost by the decomposition of the salt, and, therefore, that when placed in the desiccator, it had contained about 1·4 per cent. of moisture. Now, the amount of sulphite in the residue was 9·8 per cent. of it, or 7·28 per cent. of the damp nitrosulphate. Therefore, to recompose the salt, we have

Sodium sulphite	7·28
Nitric oxide equivalent to this	3·47
Sodium sulphate	67·05
Nitrous oxide equivalent to this	20·78
Moisture, by difference	1·42
	100·00

Sodium nitrososulphate is, therefore, an anhydrous salt, like the potassium salt. Like the potassium salt also, although it continuously decomposes into sulphate and nitrous oxide when in neutral solution, it can be heated moderately with very little change, if some sodium hydroxide is present; when, however, such an alkaline and somewhat concentrated solution is boiled, it rapidly decomposes into sulphite and nitric oxide, and this the potassium salt does not do.

It thus seems that the reversion of nitrososulphates into nitric oxide and sulphite is dependent on temperature alone, and is not prevented by the presence of water. It is otherwise with their decomposition into nitrous oxide and sulphate, which is caused either by water alone, or by elevation of temperature alone; for at the common temperature they can be kept for an apparently indefinite time when dry, but decompose in damp air or in solution; on the other hand, when heated, even in dry air, they generally decompose much more in this way than into nitric oxide and sulphate. One exception to this is the potassium silver salt, which, when heated, gives only nitric oxide and sulphite (Hantzsch). This fact points to the latter decomposition as the primary effect of heat in all cases, and to the production of sulphate and nitrous oxide as the result of the interaction of nitric oxide and sulphite. Potassium silver sulphite not being readily oxidisable, this interaction does not occur when potassium silver nitrososulphate decomposes.

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CXVI.—*The Constitution of the Nitrososulphates.*

By EDWARD DIVERS, M.D., F.R.S., and TAMEMASA HAGA, D.Sc., F.C.S.

FOLLOWING up the fact we have already made known (this vol., p. 456), that an aqueous solution of potassium nitrososulphate becomes strongly alkaline soon after the addition of alcohol to it, we have obtained results which seem to supply all that was wanting to our knowledge of the constitution of the nitrososulphates.

Some chemists have recently (*Ber.*, 1894, **27**, 1508, 3264, 3498) called these salts *nitroxysulphites*, a name which indeed points to the fact that they are produced by the union of nitric oxide and a sulphite, but ignores all else concerning them, even what was ascertained at the time of their discovery. Pelouze, in 1835, showed a keener appreciation of the nature of chemical union than the chemists referred to, and called the salts *nitrosulphates.* According to him, they are not sulphates, ordinary sulphates, that is, for they do not precipitate barium chloride (unless acidified), but are complex salts, substituted sulphates, as we should now say. Watts, in his *Dictionary*, adopting Pelouze's view, modified the name to *nitrososulphates*, in order to distinguish these salts from *nitroxyl* compounds.

After oxygenous salts had come to be regarded as oxylic compounds, sulphites were formulated as $SO(OM)_2$, in which M represents a univalent basic radicle, and in accordance with this, E. Frankland (*Lecture Notes*, 1866) expressed the sulphatic constitution of Pelouze's salts by the formula $(NO)_2{:}SO(OM)_2$, that is, he considered the sulphur to become hexavalent by uniting with two nitric oxide radicles, in place of the atom of oxygen taken up by sulphites in oxidising. Later on, as it became evident that inorganic sulphites were of one class with organic sulphonates, and that sulphites, sulphates, and thiosulphates are best formulated as $M{\cdot}SO_2{\cdot}OM$, $MO{\cdot}SO_2{\cdot}OM$, and $MS{\cdot}SO_2{\cdot}OM$ respectively, it was seen that, by analogy, nitrososulphates had to be written $M(N_2O_2)SO_2{\cdot}OM$, in which change of valency is no longer exhibited. This view of the constitution of nitrososulphates and of their relation to sulphites was advanced some 10 years ago by us in this Journal (1885, **47**, 203; see also **47**, 218).

The facts on which this view of the constitution of nitrososulphates, so far as it goes, rests seem amply sufficient. First, there is the production of the nitrososulphates in a way precisely analogous to that of sulphates and thiosulphates from sulphites, namely, by leaving a solution of a normal sulphite in contact with nitric oxide, oxygen, or sulphur, as the case requires. Then comes the reversion of nitrososulphates to nitric oxide and sulphites; not only do they, when heated in the dry state, thus decompose (Pelouze)—wholly in the case of silver potassium nitrososulphate, partly in other cases (Hantzsch)—but sodium nitrososulphate does so even in hot solution (see preceding paper). Now, this behaviour is in full agreement with what has long been known of the thiosulphates, notably of the calcium salt, which, in the first place, is producible by digesting calcium sulphite and sulphur with water at a gentle heat, and then is decomposable into these substances by boiling its concentrated solution. Lastly, sodium amalgam acts alike on solutions of nitrososulphates and thiosulphates, hyponitrite or sulphur being formed along with sulphite in either case.

What precedes refers only to the relations of the nitric oxide, as a whole, to the rest of the nitrososulphate. There remains to be considered the relations of the elements of the nitric oxide to each other and to the sulphuryl and adjacent basic radicle or metal. Putting together the constitution of hyponitrites as established by Zorn, and the generation of these salts from nitrososulphates observed by us, nitrososulphates might long long ago have been formulated as $MON_2O\cdot SO_2\cdot OM$, as indeed was done by Michaëlis in entering our results in his edition of *Graham-Otto's Lehrbuch*, but which we had hesitated to do. On the other hand, Raschig, W. Traube, Hantzsch, and Duden consider nitrososulphates to be sulphonates, from analogies which we do not find to hold good, for reasons already given in our previous paper. We have there also expressed preference for the sulphate constitution of these salts, on the ground that they instantly and fully give the reaction of a sulphate on the addition of barium chloride acidified with hydrogen chloride, since even the least stable of the certainly sulphonic nitrogen compounds discovered by Fremy take an appreciable time before a precipitate begins to form, and a not inconsiderable time for its completion. To make certain of this difference in behaviour, we have thoroughly tested, by heat under pressure, the mother liquor of barium sulphate just precipitated from potassium nitrososulphate, and have found no residual sulphur in it.

That nitrososulphates are not sulphonates, but true sulphates, can now be finally proved by the effect of alcohol on them in aqueous solution. Alone in solution, the potassium salt slowly decomposes into normal sulphate and nitrous oxide, but, when a little alcohol is present, it partly changes into potassium ethyl sulphate, potassium hydroxide, and nitrous oxide, thus:

$$(KON_2)KSO_4 + EtOH = EtKSO_4 + KOH + N_2O.$$

Potassium hydroxide and nitrous oxide are what potassium hyponitrite becomes when left dissolved in water, and may here be taken to have been derived in that way, although, as a matter of fact, we have failed to detect any hyponitrite in the solution at any point in the decomposition of the nitrososulphate; this failure, however, does not invalidate the explanation, since potassium hyponitrite in solution decomposes quite as quickly as it can here be produced. We may, therefore, express the interaction of alcohol and nitrososulphate by the equation

$$(KON_2)KSO_4 + EtOH = EtKSO_4 + KO{\cdot}N_2OH,$$

$KO{\cdot}N_2OH$ being the acid hyponitrite, the existence of which in solution was established by Zorn.

Whether hyponitrite or only alkali and nitrous oxide are the other products, the fact that potassium ethyl sulphate is formed removes all doubt as to nitrososulphates being true sulphates. Were they of sulphonic constitution, they could only yield ethyl sulphate along with hydroxylamine, hydrazine,* or ammonia, or a derivative of one of these, and then by a most improbable reaction. No such substances are found amongst the products of the decomposition.

Nitrososulphates having thus been ascertained to be true sulphates, the relations of the elements of the nitric oxide radicle can be only those shown by the formula $MO{\cdot}N{:}NO{\cdot}SO_2{\cdot}OM$. For there is nothing in the gentle act of union of the nitric oxide with the sulphite suggesting any new distribution of its elements, such as that of the oxygen of one molecule of the nitric oxide leaving it to go over to the nitrogen of the other; nothing in the properties of the nitrososulphates pointing to the presence in them of the nitroxyl radicle; nothing probable in the supposition that, in their formation, the metal or basic radicle quits the sulphur of the sulphite for the nitrogen of the nitric oxide rather than for its oxygen. On the contrary, there are the facts that metallic sodium, when it acts on them, finds in them the hyponitrite radicle (though possibly, indeed, it is formed by it), and leaves sulphite, and, again, that they are almost neutral to litmus, instead of being strongly alkaline, as they would be likely to be if their metal were in direct union with the nitrogen. The hyponitrite-sulphate formula exhibits every known chemical property of the salts, whereas a sulphonic formula explains only some of them, and suggests the existence of properties which the nitrososulphates do not possess, such as that of hydrolysing into a hydrogenised nitrogen compound.

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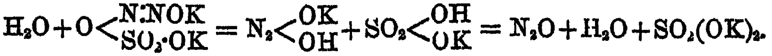
* Duden has recently ascertained that potassium nitrososulphate, when treated with sodium amalgam, yields some hydrazine (*Ber.*, 1894, **27**, 3498). It, therefore, seems probable to us that what has been taken by Maumené, ourselves, and others, to be hydroxylamine among the products of the action of sodium on nitrites, is, after all, not that substance but hydrazine.

The great rise of temperature which attends the dry decomposition of a nitrososulphate into metal sulphate and nitrous oxide must be attributed rather to the heat of nitric oxide decomposing into nitrous oxide than to the oxidation of sulphite, since this is already in the salt united to oxygen.

Nitrososulphates may be described as anhydro-double salts of hyponitrous and sulphuric acids, which in aqueous solution hydrolyse into acid hyponitrite and acid sulphate, these salts simultaneously changing into normal sulphate and hyponitrous acid (nitrous oxide and water) thus:



$$H_2O+O<{N{:}NOK \atop SO_2{\cdot}OK} = N_2<{OK \atop OH}+SO_2<{OH \atop OK} = N_2O+H_2O+SO_2(OK)_2.$$

The property they show of never exchanging their nitroso-metallic radicle for a simply metallic one when they are mixed in aqueous solution with other salts is apparently nothing more than what is seen in the true sulphate, potassium ethyl sulphate. In this connection, it is very interesting to see the nitrososulphate exchanging its specific radicle for an alkyl radicle, and thus becoming potassium or other ethyl sulphate; also to see alcohol acting as a hydroxide on an alkali sulphate. And then, along with this, as a consequence, comes the most remarkable thing of all, that by submitting potassium sulphite to the action of nitric oxide and alcohol it becomes possible to generate potassium hydroxide. That alcohol can directly give rise to potassium hydroxide by acting on any potassium salt seems an impossibility, and this furnishes a strong argument for believing that its real action on potassium nitrososulphate is what we have assumed it to be, namely, the formation of acid potassium hyponitrite, which then decomposes with water and gives the hydroxide.

The constitution of nitrososulphates, now established, shows that these salts have nothing in common with Fremy's sulphazotised salts, which are all sulphonates, and that they have some relation to the nitrosyl sulphates.

Experimental Examination of the action of Alcohol on Nitrososulphates.

Potassium nitrososulphate, in fine powder, was sealed up in a tube with absolute alcohol and kept at 100° for some hours. The two substances had no action on each other.

Some preliminary experiments made the production of potassium ethyl sulphate from an aqueous solution of potassium nitrososulphate and alcohol almost a certainty, and also enabled us to obtain in the solid state some potassium carbonate, in proof that potassium hydroxide had formed and had subsequently become carbonated by long exposure to the air. We then made two experiments, which we here describe in full, intended partly to be quantitative, but principally to afford us sufficient potassium ethyl sulphate in a pure state for thorough identification.

In one experiment, we prepared a solution containing 46·25 grams of potassium nitrososulphate in 1450 grams of 22·8 per cent. spirit, and, in the other, 14·45 grams of the salt in 212 grams of 14 per cent. spirit. Both solutions were almost saturated; we had intended the one to be spirit of 25 per cent., and the other of 15 per cent., alcohol. These solutions were left for 16 days at the summer temperature in loosely stoppered bottles, though a few days less might have sufficed for complete decomposition of the salt; potassium sulphate gradually crystallised out and nitrous oxide slowly escaped. In our previous communication to the Society, we stated that the evolution of nitrous oxide from the aqueous solution was actually arrested by adding alcohol, but that was a mistake; it goes on undiminished, but, being spread over a much longer time, becomes far less perceptible. We also observed a slight but unmistakable odour of aldehyde during the decomposition, and were just able to reduce silver by it in the solution (the alcohol used being quite free from this impurity). Its formation may, perhaps, be accounted for by supposing a minute quantity of the nitrososulphate to have decomposed into nitric oxide and sulphite, the former then acting as carrier of atmospheric oxygen to the alcohol.

The volume of the solution of the 46·25 grams of salt being so large, it was reduced to half by evaporating the solution at 70—75° in shallow, flat-bottomed, glass pans. The alkali present was then neutralised with standardised sulphuric acid, the solution made again slightly alkaline, and the evaporation continued and completed in a vacuum over sulphuric acid, occasionally interrupting the process to remove the potassium sulphate which separated.

The evaporation of the solution of the 14·45 grams of salt was effected wholly in the desiccator, that is, without the application of heat. Before evaporating, the alkali was almost neutralised with sulphuric acid.

The residue from the larger quantity of salt was extracted at an ice-cold temperature, with 5 c.c. of proof spirit, and that from the smaller quantity with 4 c.c. of proof spirit; in this way almost all the remaining sulphate was left undissolved. The spirit solution, after evaporation, gave, in the former case, 2·64 grams of crude potassium ethyl sulphate, and 1·37 grams in the latter. These quantities were necessarily only fractions of the actual quantities produced, because of the very great waste attendant on the separation of much potassium sulphate from the exceedingly soluble potassium ethyl sulphate. A true measure of the extent to which the nitrososulphate had undergone conversion into the ethyl sulphate was, however, afforded by the quantity of potassium hydroxide produced, which was estimated, by titration, in the experiment on 46·25 grams of nitrososulphate; it amounted to 1·69 grams, or 3·66 per cent. of the weight of salt taken, or about 14 per cent. of what would have been formed had the whole of the salt suffered the same change. This 1·69 grams of potassium hydroxide must have been accompanied by 4·95 grams of potassium ethyl sulphate, although we isolated little more than half that quantity, namely, 2·64 grams.

In proportion to the amount of salt taken, the yield is $1\frac{2}{3}$ greater with the 14 per cent. spirit, than where 24 per cent. spirit was used. The difference is sufficiently great to justify the belief that the formation of the ethyl sulphate is actually greater with weaker than with stronger alcohol in spite of the very imperfect means we took to collect this salt. On first consideration, it may seem that the formation of potassium ethyl sulphate must be favoured by strengthening the solution in alcohol; but this by no means follows, for it must be borne in mind that addition of alcohol greatly lessens the power of the water to dissolve the salt. Now the decomposition of the salt by alcohol is alternative to that by water, but not opposed to it; so that, in connection with the reaction with alcohol, the water may be regarded as merely the vehicle for the salt and the alcohol, and then we see that, provided these are present in molecular proportion, more alcohol can only serve to make it necessary for more water to be present so as to keep the salt dissolved, since the latter is not acted on by alcohol unless it is in solution. The more water there is present, the more attenuated is the salt exposed to the action of the alcohol. Thus, with 14·45 grams of salt in solution in 212 grams of 14 per cent. spirit, there was twice as much salt in a given volume as there was where 46·25 grams of salt were dissolved in 1450 grams of 24 per cent. spirit, while in both cases the alcohol present was far in excess of one molecule, being, even in the dilute spirit, nearly ten times the molecular quantity. Even if the chemical activity of the water is considered, still the water is present in much smaller proportion to the salt in the dilute spirit than in the stronger. The matter is interesting, but more work needs to be done in connection with it before anything can be safely concluded about it.

That the salt which we had obtained was potassium ethyl sulphate was ascertained by qualitative and quantitative tests. It was a neutral, exceedingly soluble, somewhat deliquescent salt, crystallising in pearly plates, and giving no insoluble salt with any reagent. A concentrated solution when boiled soon contained sulphuric acid; whilst a dilute solution, even when boiled for some time, remained free from it. In a solution acidified with hydrochloric acid and boiled, decomposition quickly began, but was not complete until the solution had been heated under pressure. When acidified and rapidly heated in a sealed tube at 150°, it was found to produce a little combustible gas, but when the tube was only slowly heated to 150° the decomposition into potassium hydrogen sulphate and alcohol was perfect. In all these respects, the salt we had obtained agreed with potassium ethyl sulphate.

For quantitative analysis the salt was recrystallised from water Ignited with sulphuric acid, it gave potassium sulphate equivalent to 24 09 per cent. potassium. Heated in a sealed tube with hydrochloric acid for some hours at 100°, and then for some hours longer at temperatures rising to 150°, it gave barium sulphate equivalent to 19 09 per cent. sulphur. The filtrate from the barium sulphate, evaporated to dryness and fused with potassium hydroxide, gave no additional sulphur. The alcohol formed by the hydrolysis of the salt was distilled off and easily identified as such by its odour and taste, and by the iodoform and aldehyde tests; but no attempt was made to estimate its quantity. The calculated amounts per cent. for potassium ethyl sulphate are potassium, 23·83; and sulphur, 19·52, with which our finding agrees sufficiently closely.

Imperial University,
Tōkyō, Japan.

ANNUAL GENERAL MEETING,

March 27, 1895.

Dr. ARMSTRONG, President, in the Chair.

TO-DAY I bring to a close my official connection with the Society—a connection which has been maintained during 20 years. I can only regret that it has not been in my power to render better service, but the task must ever be a terribly difficult one, even when every endeavour is made to execute it faithfully, and I am only too well aware now how much there is that might have been done with greater effect.

Although the number of Fellows is risen from 800 to very nearly 2000,* no changes in the constitution of the Society, nor in the general method of conducting its affairs, are to be chronicled; yet the period has been a very eventful one, owing to the marvellous growth of our knowledge and our more complete appreciation of the nature of chemical phenomena. We are now undoubtedly entitled to speak of chemistry as a science, but it is only too clear that very few as yet understand how complete is the mastery we have gained over matter, and that our methods are but dimly appreciated by those who are not of us,

Let me to-day first refer to the Faraday lectureship. Professor Odling, in his address to us 20 years ago, spoke of this as "an institution that in its most characteristic features is without parallel elsewhere." Further, that, "having regard to the great name with which it is associated, we cannot doubt that the nomination to this lectureship will ever be held in high esteem; and with this conviction present before us, we indulge the hope that in a long succession of Faraday lectures the Chemical Society may be as fortunate in the future as it has been in the past." The roll is certainly a very distinguished one, comprising as it does the names of

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* Although, on the day of anniversary meeting, it was not possible to announce that there were 2,000 Fellows, yet the membership had practically attained these proportions, as letters from abroad were received a few days afterwards, from gentlemen previously elected complying with the formalities required to make them Fellows, the number being thereby raised to 1999.

Dumas..........	1869	Wurtz	1879
Cannizzaro	1872	Helmholtz.......	1881
Hofmann........	1875	Mendeléef	1889

But this very fact makes the appointment one which occasions great perplexity, as experience shows that men of distinction willing to lecture and able to address us in a language which can be understood are very difficult to find. Feeling that the work done by Faraday in organic chemistry, and especially his discovery of benzene in 1825 and its consequences, had hitherto remained unnoticed, with the approval of the Council I requested Professor Emile Fischer to give the lecture, hoping that he would be willing to undertake the discussion of so interesting and important a subject; but I regret to say that he felt obliged to decline on account of his health and other reasons.

This led us to fully discuss the matter, and to arrive at the conclusion that it would be desirable to break through the practice originally initiated by the Council, and hitherto adhered to, of inviting only foreigners to deliver the lecture. Since this decision was arrived at, circumstances have arisen which have led us to take an even more novel departure. You are all aware of the separation of a hitherto unrecognised constituent from the atmosphere which Lord Rayleigh and Professor Ramsay have recently successfully effected, and you know that it is justly regarded as one of the most startling discoveries ever made in chemistry. But it is no chance discovery: on the contrary, it is the outcome of labours carried out with unwearied patience and perseverance and consummate skill, during many years past, by Lord Rayleigh. Lord Kelvin, in his Presidential Address to the Royal Society in November last, fully stated this; he pointed out how, 12 years ago, Lord Rayleigh set himself the task of re-determining the densities of the principal gases. This led him eventually to re-determine the density of nitrogen, and working in the spirit of the true philosopher, he was not content to examine only nitrogen from air, but also studied that derived from a variety of chemical changes. He was thus led to discover that nitrogen from air was very distinctly denser than that prepared by any chemical method; and, having tested the various possible explanations of the anomaly, was at last reduced to one explanation, viz., that the gas from the atmosphere was abnormally dense because it contained something denser than nitrogen. This led him, I believe, to inquire on what grounds it was assumed by chemists that atmospheric nitrogen was a uniform substance, and, eventually, to repeat the celebrated experiment described by Cavendish now 110 years ago. The initial discovery of argon was thus made—it was completed by the conjoint labours of Professor Ramsay and Lord Rayleigh, and to them chemists are indebted for the addition to our knowledge of a new substance—whether it be an element or mixture of elements or compounds, we have yet to learn—possessed of properties which make it one of the most remarkable among the host with which we are acquainted.

No chemist can fail to be impressed by Lord Rayleigh's work, and recognising its extreme value, your Council have decided to appoint Lord Rayleigh our Faraday lecturer, and to request his acceptance of the medal in recognition of the important service which he has rendered to chemistry by his discovery of *Argon.* They do not ask that he shall give any lecture, but make the award of the medal in this special manner in order to mark their sense of the value of his labours, and especially of the example he has set; we are, however, encouraged to hope that perhaps Lord Rayleigh will be prepared to address the Society on the subject of argon at an early date.

On your behalf, I have therefore now the greatest possible pleasure in presenting the Faraday medal to Lord Rayleigh.

[LORD RAYLEIGH, on receiving the medal, said that, in returning his thanks to the Society, he was somewhat embarrassed, because he felt that there ought to be another standing at his side. It was true that his researches, to which the President had referred, upon the densities of gases had rendered it almost certain that a new gas of some sort was concerned, and probable that the new gas was in the atmosphere. But from this point to the isolation and examination of argon was a long step, and the credit for it must be shared equally between Professor Ramsay and himself. In some quarters there had been a tendency to represent that antagonism existed between chemists and physicists in the matter, though such a thought never entered his mind. Professor Ramsay was a chemist by profession, while he himself had dabbled in chemistry from an early age, and had followed its development with a keen interest.]

It is not usual on these occasions to interpose other matters, but Professor Ramsay is prepared to make a communication of such special importance that I will now ask him to address you.

[Being thus called on, Professor Ramsay made the following communication of the discovery of helium in clèveite.

"In seeking a clue to compounds of argon, I was led to repeat experiments of Hillebrand on clèveite, which, as is known, when boiled with weak sulphuric acid, gives off a gas hitherto supposed to be nitrogen. This gas proved to be almost free from nitrogen; its spectrum in a Plücker's tube showed all the prominent argon lines, and, in addition, a brilliant line close to, but not coinciding with, the

D lines of sodium. There are, moreover, a number of other lines, of which one in the green-blue is especially prominent. Atmospheric argon shows, besides, three lines in the violet which are not to be seen, or, if present, are excessively feeble, in the spectrum of the gas from clèveite. This suggests that atmospheric argon contains, besides argon, some other gas which has as yet not been separated, and which may possibly account for the anomalous position of argon in its numerical relations with other elements.

"Not having a spectroscope with which accurate measurements could be made, I sent a tube of the gas to Mr. Crookes, who has identified the yellow line with that of the solar element to which the name 'helium' has been given. He has kindly undertaken to make an exhaustive study of its spectrum.

"I have obtained a considerable quantity of this mixture, and hope soon to be able to report concerning its properties. A determination of its density promises to be of great interest."]

In confirmation of this most remarkable statement, I have to request Mr. Crookes to give an account of his observations on the spectrum of the gas from clèveite.

[Mr. Crookes then spoke as follows:—

"By the kindness of Professor Ramsay I have been enabled to examine spectroscopically two Plücker tubes filled with some of the gas obtained from the rare mineral clèveite.* The nitrogen had been removed by 'sparking' over alkali. On looking at the spectrum, by far the most prominent line was seen to be a brilliant yellow one, apparently occupying the position of the sodium lines. Examination with high powers showed, however, that the line remained vigorously single when the sodium lines would be widely separated. On throwing sodium light into the spectroscope simultaneously with that from the new gas, the spectrum of the latter was seen to consist almost entirely of a bright yellow line a little to the more refrangible side of the sodium lines, and separated from them by a space a little wider than twice that separating the two sodium components from one another. It appeared as bright and as sharp as D_1 and D_2. Careful measurements gave its wave-length 587·45, the wave-lengths of the sodium lines being D_1 589·51 and D_2 588·91. The differences are therefore—

	Wave-lengths.	Differences.
D_1	589·51	
		0·60
D_2..................	588·91	
		1·46
New Line	587·45	

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* Clèveite is a variety of uraninite; chiefly a uranate of uranyle, lead, and the rare earths. It contains about 13 per cent. of the rare earths, and about 2·5 per cent. of a gas said to be nitrogen (*Bull. U. S. Geol. Survey*, 78, 43—79).

"The spectrum of the gas is therefore that of the hypothetical element helium, or D_3, the wave-length of which is given by Ångstrom as 587·49 and by Cornu as 587·46.

"Besides the helium line, traces of the more prominent lines of argon were seen.

"Comparing the visible spectrum of the new gas with the band and line spectrum of nitrogen they are almost identical at the red and blue end, but there is a broad space in the green where they differ entirely. The helium tube shows lines in the following positions.

		Wave-length.	
(*a*.)	D_3, yellow............	587·45	Very strong. Sharp.
(*b*.)	Yellowish-green	568·05	Faint. Sharp.
(*c*.)	Yellowish-green......	566·41	Very faint. Sharp.
(*d*.)	Green	516·12	Faint. Sharp.
(*e*.)	Greenish-blue	500·81	Faint. Sharp.
(*f*.)	Blue................	480·63	Faint. Sharp.

"I have taken photographs of the spectrum given by the helium tube. At first glance the ultra-violet part of the spectrum looks like the band spectrum of nitrogen, but closer examination shows considerable differences. Some of the lines and bands in the nitrogen spectrum are absent in that from the helium tube, whilst there are many fine lines in the latter which are absent in nitrogen. Accurate measurements of these lines are being made."]

I am sure you will agree that we must all congratulate Professor Ramsay on a discovery of such extraordinary importance and interest.

To return to my address, I have so fully dealt with the general questions which affect the Society in my previous address, that little is to be said on such matters on the present occasion. Outwardly, the year has passed quietly; but important questions have been under discussion, which certainly have given some of us much cause for thought, if not anxiety.

We have lost an old and faithful servant and friend in our collector, Mr. Hall, who last summer retired on a pension from the Society after being 25 years in our employ. All who are in the habit of attending the Society's rooms will have missed his kindly presence. Our Treasurer was successful in collecting a sum of over £30 from the members of the Council, which was expended in the purchase of a time-piece and silver tea service—which were presented to Mr. Hall and his wife—and of articles of jewellery, which were presented to his two daughters, to whom and to Mrs. Hall the Society is under obligation for their attendance in the tea room. Needless to say, the family have expressed their great gratification at receiving these marks of recognition.

The opportunity has been taken to institute changes in the paid staff of the Society, which have long been advocated by the officers, but postponed mainly on financial grounds. A Committee of the Council, after long deliberation, presented a report, which was adopted by the Council, recommending the appointment of an Assistant Secretary, who should also act as an assistant to the Treasurer and as Librarian, a collector being no longer necessary now that money is so universally transmitted by post. The Council have been fortunate in securing the services as Assistant Secretary of Mr. Robert Steele, formerly a Science Master at the Bedford Modern School. They have furnished him with a junior assistant to aid in the work of the library.

The fusion of the offices of Assistant Secretary and of Librarian, effected with the object of securing the constant attendance of the Librarian, has led to the termination of Dr. Thorne's official connection with the Society, and I desire on this occasion, on behalf of the Council, to express our warmest thanks to Dr. Thorne for the assistance he has rendered us as Librarian since the death of Mr. Watts in 1884.

As to our numerical strength, the statistics are by no means satisfactory, the number of those who have a right to appear as Fellows of the Society being not very many more than last year, owing to the unusually large number removed on account of their failure to comply with our bye-laws and the Treasurer's just demands. Although our bye-laws, when strictly interpreted, allow us to strike off those who have left three years' subscriptions unpaid, a lax practice has grown up of waiting until four years' arrears are owing. By order of the Council, the names of 23 Fellows are removed from our register who owe four annual subscriptions, and also of 27 who are three years in arrears, making a total of 50. The names of those thus removed are as follows.

Four years in arrear:—Cook, H. J.; Chenhall, J. W.; Chiddey, A.; Cunningham, A. A.; Donovan, H. T.; Evans, G. T.; Featherstone, W. B.; Farquharson, A. C.; Gregory, W.; Gee, W. W. H.; Holt, C. G.; Haslam, A. R.; Maybury, C.; Moos, N. A. F.; Morgan, A. F.; McCalman, G.; Porter, H.; Stanley, T. W.; Shaw, H. G.; Tarn, A.; Trinks, C. H.; Wood, G. W.; Wade, M. S.

Three years in arrear:—Broughton, F.; Brunker, J. E.; Bailey, R. D.; Byrn, G.; Barry, T. D. C.; Belbin, T. St. J.; Coleman, T. H.; Davies, A. E.; Davies, J.; Gracey, R.; Grey, W. T.; Gerrans, B. H.; Hori, E.; Irons, H. E. J.; Jenner, T.; Kilpatrick, C.; Knowles, J.; Linnell, A.; Luckett, A. H.; Menzies, Rev. T. J.; Parry, J.; Pike, A. E.; Serre, C. A.; Tompkins, H. R.; Whitlock, J.; Wilkie, J.; Wadsworth, G. H.

In order, as far as possible, to minimise the difficulties which arise from long-continued failure to comply with our rules, the Council recommend an alteration in the bye-law relating to payments by Fellows.

It has been customary to send out the Journal even to Fellows who are several years in arrear, but in order to more effectually draw attention to our rules and to prevent loss, the Council have ordered that in future the Journal shall not be supplied to Fellows one year in arrear.

The following 27 Fellows have withdrawn from the Society.

Auerbach, G.; Bell, Sir W. J.; Cortis, A. B.; Day, A. W.; Dott, D. B.; Forth, H.; Greenish, H. G.; Hall, E.; Jackson, J. R.; Lauer, W. E.; Lightbown, J. H.; Mason, G. B.; Muller, Prof. G.; Oxford, Rev. A. W.; Parker, G. L.; Paterson, J. R.; Peace, F. K.; Peterson, F. W.; Platts, K.; Ray, W., Samuel, A. H.; Shaw, H. D.; Stavert, Rev. W. J.; Stoker, H.; Sutcliffe, S.; Taylor, G. S.; Venis, W.

We are fortunate in having been deprived of only 17 of our Fellows by death, viz., the following:—Ashwell, J. R.; Barratt, Alex.; Beauchamp, Maj.; Board, G.; Carteighe, J.; Dunne, B. L.; Evans, P. N.; Gill, C. H.; Hughes, F. R.; Johnson, F. R.; Morris, J. E.; Nason, Prof. H. B.; Salet, G.; Thornthwaite, W. H.; Twining, A. H.; White, A.; Wright, C. R. A.

We must especially regret the decease of one of these, Dr. Alder Wright, at so early an age; men gifted with so much originality and versatility and with such extraordinary powers of work, are at all times rare, and we can ill afford to lose them. It is noteworthy at the list contains the name of one of our original Fellows, F. R. Hughes, so that now but one remains -the evergeen Lord Playfair, although the equally active Sir Henry Gilbert is very nearly of the same standing in the Society.

In tabular form, the corrected statistics of membership are as follows.

Number of Fellows, March 31st, 1894		1962
,, ,, since admitted		131
		2093
Removed on account of non-payment of four annual subscriptions	23	
Do. three annual subscriptions	27	
Withdrawn	27	
Deaths	17	
	—	94
Number of Fellows, 1895		1999
Foreign Members		30

I have been favoured with the following

OBITUARY NOTICES.

GREGORY BOARD died suddenly on April 29, 1894, at Port Pirie, South Australia, where he was Superintendent of the Broken Hill Proprietary Works. He was born on July 21, 1846. He studied at the School of Mines and the Birkbeck Institute, and was a fellow student with Sydney Gilchrist Thomas in Mr. Chaloner's classes in 1870–72, at which time he was engaged as an "attendant" (not "assistant") at the British Museum, under Professor Maskelyne and Dr. Flight, being a good mineralogist. Giving up the position on account of the difficulties in the way of promotion, he left England for America in 1872, and until 1875 was engaged in coal-mining in the State of Illinois. Thence he was attracted to the silver mines of Colorado, and was appointed Professor to the School of Mines. He also held prominent positions on the staff of some of the most important mines, but he resigned these positions, and entered the smelting business with other partners. As he suffered from the effects of lead-poisoning, he entered the cattle-raising business with a view to recruiting his health, and on his recovery he again took up smelting at Denver, Colorado. He left America to accept the management of the Australian Smelting and Refining Works at Dry Creek, having been selected for this position by the British Consul at San Francisco, entering on his duties in 1887. On arrival, Mr Board was appointed Consulting Manager for the Commodore Vanderbilt Gold and Silver Mining Company, and Consulting Metallurgist for the British Broken Hill Proprietary Company. In August, 1890, he left Dry Creek and came to Port Pirie as Superintendent of the Refinery and Manager of the British Broken Hill Company's smelting works there. When the latter company disposed of their property to the proprietary Company, Mr. Board was appointed Superintendent of both smelters and refinery, and held the position until his death. The deceased was a foundation member of the Australian Institute of Mining Engineers, Fellow of the Royal Society of South Australia, besides being intimately associated with several other scientific societies.

JOHN CARTEIGHE, of the firm of Dinneford and Co., died at his residence, 3, Hereford Square, S.W., on April 1, 1894, of heart disease, from which he had suffered during many years. He was originally intended for the legal profession, but becoming interested in chemical science, left the law and, through the introduction of a friend, became one of Faraday's assistants at the Royal Institution. This position he relinquished on the invitation of Mr. Dinneford, with whose pharmacy and manufactures he was thereafter associated until his death at the age of 69.

PHILIP NORMAN EVANS, Ph.D., son of Sir John Evans, K.C.B., F.R.S., born 13th December, 1854, and dying 9th December, 1893, leaves behind him the pathetic interest which attaches to a career suddenly cut short as it was opening out into paths of distinction and wide usefulness. He received his early education at Harrow, and from school passed directly into the routine life of the paper mills with which his family are connected. Subsequently he went over to the United States, travelling through the mining districts of the west, afterwards taking up residence in the Eastern States, continuing his technical studies in a paper mill. The period 1884–85 was spent at Harvard, chiefly in the study of chemistry, which he continued at Bonn during 1885–88, acting for some time as private assistant to Professor Wallach. In 1889, he graduated Ph.D. at Erlangen, his thesis embodying the results of an investigation of antimony pentachloride, its hydrates, and its interaction with oxalic acid. Of his career at Bonn there are other substantial records, amongst which may be mentioned a most flattering "testimonial" from Kekulé, who evidently regarded him as a young man of exceptional promise. After graduating, he returned to London, and started a practice as consulting and analytical chemist, at 28, Great Ormond Street. Here he was joined in partnership in the following year by Dr. Wirtz, of Bonn, and the foundations were rapidly laid of a flourishing practice. Of his professional work it would be gratuitous to say more than that it was marked by the practical skill, the precision of the trained experimentalist, and the judicial honesty of a man starting in life with the best traditions and schooled in the uncompromising methods of science.

Evans was, of course, greatly interested in the technology of paper making, which he had mastered in its fullest detail. His interest in the subject is shown by his careful translation of Hertzberg's work on *Paper Testing*, a description of the methods adopted at the German Government Testing Station at Charlottenburg. This work he published in 1892.

Such is a brief sketch of the making of a career destined to be cut short in the very springtime of promise. The close of his life was marked by a manful struggle against the malady to which he fell a victim at the early age of 39.

CHARLES ROMLEY ALDER WRIGHT was born in 1844, and was the youngest child of Romley Wright, a civil engineer, who was at one time employed on the Ordnance Survey of this country. His education was undertaken by his father until 1861, when young Wright joined Owen's College, where he quickly distinguished himself in the classes connected with chemistry, physics, mathematics and classics. His first piece of original work was done under Roscoe's direction, and was published in the Journal of our Society in 1866, under the title "Action of Light on Sensitive Photographic Papers." In the same year Wright was appointed to the post of chemist at the Weston Works of the Runcorn Soap and Alkali Company, where he remained about a year, during which time he published several papers bearing on the alkali manufacture. In 1867 he became assistant to Dr. Bernays in the chemical laboratory at St. Thomas's Hospital, and in the following year joined Matthiessen in a similar capacity at St. Mary's Hospital. Matthiessen and Wright jointly contributed to the Royal Society four papers on "The Derivatives of Opium Alkaloïds." One of the most important pieces of work in connection with which their names will always be associated was the discovery of apomorphine, which, as a rapid and powerful emetic, has proved a most valuable adjunct to medical practice. From 1869—1871, Wright was associated with Sir Lowthian Bell in a series of elaborate investigations on the chemistry of iron smelting. In 1871 he was appointed lecturer on chemistry and physics in St. Mary's Hospital Medical School, which post he occupied up to the time of his death. During his connexion with St. Mary's, he carried out and published, both alone and in conjunction with various collaborateurs, a large number of important researches, some of the principal of which are mentioned in the following list.

Nine papers on Derivatives of Morphine and Codeïne to the Royal Society (1871—1874); six papers on Isomeric Terpenes to the British Association Reports (1873—1877); six papers on the Action of Organic Acids and their Anhydrides on Natural Alkaloïds to the Chemical Society (1874—1880); seven papers on Narcoïne, Narcotine, Cotarnine, and Hydrocotarnine to the Chemical Society (1874—1877); four papers on Alkaloïds of the Aconites to the British Association Reports (1877—1879); three papers on the Alkaloïds of the Veratrums to the British Association Reports (1878—1879); a series of Reports on Chemical Dynamics to the Chemical Society (1878—1880); nine papers on the Determination of Chemical Affinity in terms of Electromotive Force to the Physical Society (1877—1885). During the latter years of his life, Wright devoted considerable attention to the study of alloys, and contributed a series of papers on the subject to the *Proc. Roy. Soc.* He also wrote a number of articles on matters of technological interest, including a series of articles on Coal Tar Distillation and Products in *Muspratt's Dictionary;* another series on Soap, Sulphur, and Sulphuric Acid in *Thorpe's Dictionary of Applied Chemistry*; four lectures on Metals and their Industrial Applications delivered at the Royal Institution (1878); articles on Iron, Steel, &c., in the *Encyclopædia Britannica* (1879–81); three Cantor lectures on the Manufacture of Toilet Soaps to the Society of Arts (1885); several articles to the *Journal of the Society of Chemical Industry*. In addition, Wright wrote a book for general readers, entitled *The Threshold of Science*, and another on *Oils, Fats, and Waxes*.

Wright was an original member of the Institute of Chemistry, and of the Physical Society. He was elected a Fellow of the Royal Society in 1881. He was a D.Sc. of the London University, and B.Sc. of the Victoria University. Although reference to many of the branches of original work undertaken by Wright has been omitted, yet, from the brief account given, sufficient indication can be obtained of his remarkable productiveness and versatility as an original enquirer. His indefatigability is the more striking when it is borne in mind that from a boy he had suffered from disease of the hip, which was constantly the cause of severe suffering to him, but which he never allowed to interfere with the geniality and kindness of manner that won for him so many friends. Of late years the lameness due to the hip disease prevented his taking sufficient exercise, but his friends were quite unprepared for the sudden development of diabetes, which rapidly caused diabetic coma, and carried him off on July 25, 1894, when he had barely attained his forty-ninth year.

We have to deplore the loss of no fewer than three of our foreign members—Marignac, v. Helmholtz, and Josiah P. Cooke.

As Marignac's name was so intimately connected with the rare earths, we have requested our foreign member, Professor Cleve, who is one of the chief authorities on the chemistry of this group, to deliver the Marignac memorial lecture, and especially to prepare a monograph giving a critical account of the present state of knowledge of the rare earths. As the anniversary of Marignac's death falls on Easter Monday, it is impossible to meet on that day, and it is a question whether Professor Cleve will be able to attend here; but he has been good enough to transmit the manuscript of his lecture to the Treasurer, and should he be unable to come over, this will be printed in the Journal.*

Von Helmholtz has done work of special interest to chemists in two directions—in connection with electrolysis and with the theory of vortex atoms. I am glad to say that Professor Fitzgerald, F.R.S., has been good enough to undertake to deal specially with these questions in a memorial lecture on v. Helmholtz.

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* This appeared in the June No. of the Transactions, p. 468.

Arrangements are yet to be completed to obtain a proper discussion of the field of chemical work to which Professor Cooke specially directed his attention.

I may state that I have devoted much time to the preparation of an account of certain sections of Hofmann's work not touched by the addresses delivered by Lord Playfair, Sir F. Abel and Dr. Perkin, and now that I am relieved from the cares imposed by my office, I anticipate being able very soon to complete this for publication, together with the other notices. I may add that during the past three years I have devoted all my leisure to the preparation of an account of the Society's work, including an analysis of its publications during the past 50 years of its existence; this has been a task of no slight difficulty, and I have been unwilling to issue it in any but a complete form, but I am glad to say that I have now all but completed it.

Our Assistant Secretary has been engaged in verifying our register of Fellows, and as illustrating the difficulties in the way I may mention that no fewer than 51 Life Fellows have not responded to the request for their present addresses. The addresses of 6 Life Fellows and 6 others are unknown beyond question, journals sent to their registered addresses having been returned through the post.

The fact that 564 books have been issued from our library during the year is evidence that good use is being made of it. Its growth is shown by the following statistics :—

	March 22nd, 1894.	Additions in 1894–95.	Present State.
Volumes of systematic works..........	3,512	85	3,597
Volumes of periodicals...............	6,678	120	6,798
Volumes of duplicate periodicals for circulation	1,404	31	1,435
Pamphlets........................	2,273	35	2,308
	13,867	271	14,138

I would again point out that there is abundant opportunity for Fellows generally to co-operate in making our library as complete as possible by presenting works and by making suggestions.

I regret to say that a somewhat virulent outbreak of the black-balling mania affected one of our elections. I have been at the pains to make special inquiries with reference to those who were rejected, and am satisfied that, in the majority of cases, they were the victims of unjust prejudice; it ought not to be necessary to point out how detrimental to our interests any attempt must be to introduce personal considerations into such questions.

The number of new Fellows admitted into the Society during the year is far fewer than last year—118 instead of 140—but this, unfortunately, is due to the fact that 23 of those elected have as yet failed to satisfy the conditions on which admission into the Society is granted.

As to our scientific activity, the number of communications made to us during the year, of which records appear in the Proceedings, is 132.

The volume of Transactions published in 1894 contains 83 papers, occupying 1,039 pages, many of which undoubtedly possess very considerable value, and the variety of subjects treated of is surprising. The number is somewhat considerably fewer than last year, when 104 papers were printed in the Transactions, but in these days of over-production and premature publication this is not necessarily to be deplored.

The average length of a paper during the past two years has been about 12 pages. I venture to think that this is far too much, and that, as I pointed out last year, much might be done with advantage to shorten papers.

The following statistics relate to our Abstracts.

	Pages.	No. of Abstracts.
PART I.		
Organic Chemistry	631	1105
PART II.		
General and Physical Chemistry		245
Inorganic Chemistry		218
Mineralogical Chemistry		99
Physiological Chemistry		163
Chemistry of Vegetable Physiology and Agriculture		99
Analytical Chemistry		328
Total in Part II	492	1152
Total in Parts I and II	1123	2257

The number of papers abstracted was 389 fewer than in the previous year, when the number was abnormally large, but the subject index is larger than ever, occupying no fewer than 100 pages.

I need scarcely say that the Council very fully recognise the great value of the work which is done for the Society by both the Editor and the Sub-Editor in connection with our Journal.

I may mention that Mr. Cross has called the attention of the Council to the desirability of printing our Journal on paper of a higher quality, and that this question is being carefully inquired into by the Publication Committee.

Bearing in mind the increase in the size of our Journal, and its great value, the Council have resolved to increase the sale price to 40*s*. per annum after this year.

It is a cause of congratulation that the Physical Society has at last been led to follow our example and to publish abstracts of physical papers. We can heartily wish them success, as the work they do will be of the greatest value to us. At present they are working on a very modest scale, which they will perforce find disproportionate to the demands that will inevitably be made on them. I imagine it will be for us and others outside the Physical Society to make it possible for them to carry on the enterprise with all necessary completeness. I regard the appearance of the Society at Burlington House as a step of great importance, as marking the recognition by public opinion of the extreme value of physics. I am sure it has given us great pleasure to receive them as guests, and to arrange that their meetings may take place in our rooms.

It is also a fortunate circumstance that during the year the various Brewing Institutes have undergone amalgamation, and that the Federated Institutes now publish a journal containing a record of their transactions, as well as abstracts of papers of special interest to brewers, which promises to be of great value to those concerned in the industry. I trust that this is but the preliminary step towards that wider affiliation with the Society of Chemical Industry to which I referred in my previous address (Trans., 1894, 349), whereby *all* in this country who are concerned in the application of chemical science to industry will be brought into direct and active co-operation.

No happier augury of advancement towards that ideal union of the Anglo-Saxon race in the field of science, on which I dwelt last year, could be wished for than is afforded by the recent establishment of a New York section of our Society of Chemical Industry We must foresee that the gravest competition in the chemical industries which we shall be called on to encounter in the future will arise from their extension in America: it is therefore desirable that the most amicable relations possible should be established, in order that the rivalry may be as far as possible deprived of the elements of bitterness which too easily attend such struggles. Perhaps the step may not be without effect in promoting the union of workers in pure chemistry in America at least, if not as well of those in America with those in this country.

In June last, by the courtesy of the Managers, we were enabled to hold a special meeting at the Royal Institution, when an account was given by Professor Dewar of observations on phosphorescence and photographic action at very low temperatures. Professor Dewar was enabled to give what was to many a novel and very interesting demonstration of the use of liquid oxygen as a refrigerating agent. We have often been indebted to the Institution for the use of its lecture room, but on this occasion a novel departure was made, and we have to thank the Managers as well as Professor Dewar for having so liberally placed the resources of the Institution at the disposal of our Society.

The technical portion of my address, on "The Nature of Chemical Change and the Conditions which determine it," is so lengthy and so full of detail that I beg that it may be taken as read:—

SIR FREDERICK ABEL thereupon proposed a vote of thanks to the President, coupled with the request that he allow his address to be printed. Dr. W. H. Perkin seconded the motion, which was carried by acclamation. The President having thanked the meeting,

Professor THORPE, the treasurer, gave an account of the balance sheet, which he laid before the Society, duly audited.

The receipts had been:—By admission fees and subscriptions, £4049; by sale of Journal and advertisements, £470 15*s.* 6*d.*; and by dividends on invested capital, £364 17*s.* 6*d.* The expenses had been:—On account of the Journal, £2757 5*s.* 3*d.*; on account of the Proceedings, £239 17*s.* 3*d.*; on account of the General Index, £112 19*s.* 2*d.*; on account of the Library, £319 4*s.* 2*d.*; the total expenditure being £4135 9*s.* 11*d.* Grants amounting to £197 had been made to Fellows from the Research Fund during the year.

Dr. GLADSTONE proposed that the thanks of the Fellows be tendered to the treasurer for his services during the past year; this motion was seconded by Mr. Carteighe.

The vote of thanks to the treasurer having been passed, Professor Tilden proposed a vote of thanks to the Council and officers.

Mr. Hehner supported the motion, which was adopted.

The Treasurer, in responding, proposed a vote of thanks to the auditors. Mr. Friswell seconded the motion, which was unanimously adopted, and acknowledged by Mr. Bevan.

Mr. Warrington proposed a vote of thanks to the Editor, Sub-Editor, and Abstractors, which was seconded by Dr. Wynne and carried. Mr. Groves briefly responded.

Scrutators were appointed, and a ballot was then taken for the election of officers and Council for the ensuing year; the following were subsequently declared elected:—

President: A. Vernon Harcourt, M.A., LL.D., D.C.L., F.R.S.

Vice-Presidents who have filled the office of President: Sir F. A. Abel,

Dr. THE TREASURER IN ACCOUNT WITH THE CHEMICAL SOCIETY FROM MARCH 16TH, 1894, TO MARCH 16TH, 1895. Cr.

	£	s.	d.	£	s.	d.
Balance at Bank March 16th, 1894	1,842	1	10			
,, in hands of Treasurer	0	9	10			
				1,842	11	8
Receipts by Life Compositions, Admission Fees, and Subscriptions from March 16th, 1894, to March 16th, 1895.						
18 Life Compositions at £20	360	0	0			
3 ,, ,, balance of, at £18	54	0	0			
136 Admission Fees at £4	544	0	0			
29 Subscriptions for 1892 at £2	58	0	0			
1 ,, ,, 1892 at £2, balance of (resigned)	1	0	0			
115 ,, ,, 1893 at £2	230	0	0			
2 ,, ,, ,, at £1	2	0	0			
482 ,, ,, 1894 at £2	964	0	0			
8 ,, ,, ,, at £1	8	0	0			
904 ,, ,, 1895 at £2	1,808	0	0			
20 ,, ,, ,, at £1	20	0	0			
				4,049	0	0
Sale of Journals	459	11	6			
,, Proceedings	5	9	0			
Proceeds of advertisements in Journal	5	15	0			
				470	15	6
Subscriptions from the Society of Chemical Industry to June, 1894	10	10	0			
,, ,, Society of Public Analysts to Jan. 1st, 1895	14	14	0			
,, ,, Physical Society to Jan. 1st, 1895	6	16	6			
				32	0	6
Repayment of Income Tax				7	2	6
Year's Dividends on £6,730 Metropolitan Board of Works 3½ per cent. Stock	227	18	11			
Year's Dividends on £4,000 Consols	106	9	0			
Year's Dividends on London and North Western Railway Debenture Stock	30	9	7			
				364	17	6

	£	s.	d.	£	s.	d.
Expenses on Account of the Journal.						
Salary of Editor	275	0	0			
Salary of Sub-Editor	175	0	0			
,, Sub-Editor's Assistant	8	2	9			
Editor's Postages	5	11	2			
Abstractors' Fees	254	8	11			
Periodicals for Abstractors	12	16	6			
Printing of Journal	1,622	9	11			
Distribution of Journal, by Printers	338	14	8			
,, ,, by Society	3	15	1			
Authors' Copies	61	6	3			
				2,757	5	3
Collotype portraits of the late Professor von Hofmann				42	10	0
Printing of Proceedings (including 1892 Index)	171	19	7			
Distribution of Proceedings	67	17	8			
				239	17	3
Publishers' Commission				47	4	6
Expenses on Account of the General Index.						
Salaries	105	16	10			
Petty expenses	7	2	4			
				112	19	2
Expenses on Account of the Library.						
Salary of Librarian	37	10	0			
,, Library Attendant	9	17	6			
Books and Periodicals	183	19	4			
Binding	87	17	4			
				319	4	2
Salary of Assistant Secretary				62	10	0
,, Mr. Hall				46	10	0
Pension to Mr. Hall (5 months)				54	3	4
Cheque Book and Special Printing (Bank)				1	4	6
Miscellaneous Printing				87	11	11
Stationery				43	12	9
Subscription to the Lavoisier Fund				25	0	0
Congratulatory Address to Dr. C. R. Fresenius				4	7	10
House Expenses.						
Providing Refreshments	13	16	6			
Lighting the Building (gas, £26 0 6; electric light, £21 0 6)	47	1	0			
Heating ,, (coals)	15	14	8			
Cleaning ,,	10	0	0			
Repairs	16	16	9			
Fitting up Electric Bells	4	17	6			
Petty House Expenses	8	7	1			
House Porter's Wages	66	5	0			
,, ,, Uniform	6	10	0			
Annual Fee to Gate Porter	2	2	0			
Inhabited House Duty	0	6	3			
				191	16	9

1895. Mar. 16. *Assets.*	£	s.	d.	£	s.	d.
Balance at Bank (current account)	1,630	5	9			
" " (on deposit)	1,000	0	0			
" in hands of Treasurer	0	12	0			
Metropolitan Board of Works 3½ per cent. Stock	6,730	0	0			
3 per cent. Consols	4,000	0	0			
London and North Western Railway Converted Stock	1,050	0	0			
				6,766	7	8

	£	s.	d.
Collector's Commission on Subscriptions (5 per cent. on £1,298)	64	18	0
Bankers' Commission	0	19	2
Treasurer's Stamps and Drafts	5	16	10
" Petty Cash Disbursements	0	3	4
" Assistant	10	0	0
Mr. Hall's Postage Account	13	2	6
Secretarial Postages	4	12	8
Balance at Bank (current account)	1,630	5	9
" in hands of Treasurer	0	12	0
" at Bank (on deposit)	1,000	0	0
	6,766	7	8

Audited, with vouchers, and found correct.
March 16th, 1895.

Edward Bevan.
E. W. Voelcker.
Bertram Blount.

The Treasurer of the Chemical Society in Account with the Research Fund.

From March 16th, 1894, to March 16th, 1895.

Dr.

1894.		£	s.	d.
Mar. 16.	Balance at Bank	164	16	9
	Year's Dividends on £4,400 Metropolitan Board of Works 3½ per cent. Stock	149	0	7
	Year's Dividends on £1,000 North British Railway 4 per cent. Stock	38	15	7
		£352	12	11

1895. Mar. 16. *Assets.*	£	s.	d.
Balance at Bank	134	2	11
Metropolitan Board of Works 3½ per cent. Stock	4,400	0	0
North British Railway 4 per cent. Stock	1,000	0	0
	£5,534	2	11

Cr.

			£	s.	d.
Mar. 30th, 1894.	Honorarium with Longstaff Medal to Mr. Horace T. Brown		20	0	0
Apr. 22nd "	Mr. John Pinches: Striking Medal		1	10	0
July 2nd "	Grants to A. E. Tutton	£47			
" "	" Dr. Jas. Walker	10			
" "	" Herbt. Jackson	25			
" "	" W. A. Bone	10			
" "	" Dr. Geo. Tate	20			
" "	" W. R. Dunstan	20			
			132	0	0
Jan. 22nd, 1895.	" J. J. Sudborough	10			
" "	" H. Crompton	20			
" "	" F. D. Chattaway	10			
" "	" W. H. Perkin, jun.	25			
			65	0	0
	Balance at Bank		134	2	11
			£352	12	11

Audited, with vouchers, and found correct.
March 16th, 1895.

Edward Bevan.
E. W. Voelcker.
Bertram Blount.

Bart., K.C B, D.C.L., F.R.S.; H. E. Armstrong, LL.D., Ph.D.; F.R.S.; A. Crum Brown, D.Sc., F.R.S.; W. Crookes, F.R.S., E. Frankland, D.C.L., F.R.S.; Sir J. H. Gilbert, Ph.D., F.R.S.; J. H. Gladstone, Ph.D., F.R.S.; H. Müller, Ph.D., F.R.S.; W. Odling, M.B., F.R.S.; W. H. Perkin, LL.D., Ph.D., F.R.S.; Lord Playfair, K.C.B., Ph.D., F.R.S.; Sir H. E. Roscoe, LL.D., F.R.S.; W. J. Russell, Ph.D., F.R.S.; A. W. Williamson, LL.D., F.R.S.

Vice-Presidents: E. Atkinson, Ph.D.; Horace T. Brown, F.R.S.; F. R. Japp, M.A., Ph.D., LL.D., F R.S.; Ludwig Mond, F.R.S.; C. O'Sullivan, F.R.S.; W. C. Roberts-Austen, C.B., F.R.S.

Secretaries: J. M. Thomson; W. R. Dunstan, M.A., F.R.S.

Foreign Secretary: Raphael Meldola, F.R.S.

Treasurer: T. E. Thorpe, LL.D., F.R.S.

Other Members of Council: P. P. Bedson, D.Sc.; B. H. Brough; H. B Dixon, F.R.S.; Bernard Dyer, D.Sc.; R. J. Friswell; O. Hehner; F. S. Kipping, Ph.D., D.Sc.; H. McLeod, F.R.S.; W. A. Shenstone; T. Stevenson, M.D.; W. P. Wynne, D.Sc.; S. Young, D.Sc., F.R.S.

The nature of chemical change and the conditions which determine it.*

> "All the facts show us that that power commonly called chemical affinity can be communicated to a distance through the metals and certain forms of carbon; that the electric current is only another form of the forces of chemical affinity; that its power is in proportion to the chemical affinities producing it; that when it is deficient in force it may be helped by calling in chemical aid, the want in the former being made up by an equivalent of the latter; that, in other words, *the forces termed chemical affinity and electricity are one and the same*."†—Faraday's *Experimental Researches in Electricity*, 1834, Series VIII, § 918.

Foremost among the problems to which during recent years attention has been devoted is that of the nature of chemical change. Whilst English workers especially have made most important contributions to our knowledge of the conditions under which change will occur,‡ foreign workers have been most active and successful in developing mathematical methods of treating the subject. Indeed, the statement recently made in a prominent chemical journal that "it has certainly become impossible to read chemical theory without a working knowledge of the calculus" is a striking comment on the alterations in the conditions under which the chemist will work in the future, which must serve to remind us how very different a preparation students must now undergo if they desire to thoroughly master the theories of our science.

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* Time did not permit of my giving an account of this portion of my address at the Anniversary Meeting. It deals with a very difficult subject, and, on revising the draft, I could not but feel that there was much in it that might be improved; but as such work could not be done effectively at a time when thoughts of other subjects filled the mind, I have waited until the long vacation to carefully reconsider it. Although still dissatisfied with my statement as a clear and complete picture, I venture to put it forward in the hope of calling attention to the numerous important considerations awaiting discussion.

† The italics are Faraday's own.

‡ Compare H. B. Baker (Trans., 1894, 623), where a list of investigations on the influence of moisture on chemical change is given; H. B. Dixon, *Journ. of Gas*

The subject first came under consideration in this Society just ten years ago. In the discussion on Mr. Brereton Baker's paper on combustion in dried gases (compare Proceedings, 1885, 37), I ventured to insist that the evidence that action did not take place between two substances was so strong that chemists would ere long be forced to form a definite conception of the nature of chemical action and of the conditions under which chemical action could take place; and I then pointed out that physicists were in advance of chemists, drawing attention to Ayrton and Perry's paper on the contact theory of voltaic action, in which it is directly stated that Ohm's well-known law is equally applicable to electrical and chemical changes.*

On the occasion in question I defined chemical action as *reversed electrolysis*, and explicitly stated that in any case in which chemical action is to take place it is essential that the system operated on shall contain a material of the nature of an electrolyte. The expression "chemical action" was used as including all cases of exothermic change, cases of endothermic change being obviously comparable with direct electrolyses, as in all such cases energy from without must be impressed on the system.

Later in the year, at the British Association meeting at Aberdeen, in my address to the chemical section, I discussed the matter more fully, and then stated in so many words that the conditions which obtain in any voltaic element are those which must be fulfilled in every case of chemical action. I carefully pointed out, however, that there was nothing new in this, and to justify my assertion drew

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Lighting, 1881, 37, 704, "On the oxidation of sulphur dioxide;" W. J. Russell, *J. Chem. Soc.*, 1874, 3, "On the action of hydrogen on silver nitrate;" V. H. Veley, *Phil. Trans.*, A., 1891, 279, "The conditions of chemical change between nitric acid and certain metals."

* "Hitherto chemists have only employed the two ideas of chemical affinity and the amount of chemical action, but we have shown that these ideas are simplified when regarded as electromotive force of contact and currents of electricity. To connect the two ideas we have a third, viz., *resistance*, and the electrical law of Ohm becomes the chemical law—*the quantity of chemical action in unit time equals the sum of a great number of terms, each of which is an electromotive force divided by a resistance.*" (Ayrton and Perry, *Proc. Roy. Soc.*, 1887, 27, 227).

attention to various passages in Faraday's *Experimental Researches in Electricity*, in which such a doctrine is laid down in the clearest possible terms.* Let me here again say that nothing is to me more surprising than the continued disregard of Faraday's teaching on this subject. We know that in regard to purely electrical questions, even in this country, it was not until Clerk Maxwell came forward as his interpreter that attention became rivetted upon his conceptions; and abroad, even Clerk Maxwell was disregarded until Hertz's experimental demonstration ensured that respect being paid to his pleadings which they were so long denied. Faraday's views regarding chemical action have never yet received proper notice, although the language in which they are expressed is so simple and direct that they cannot be misunderstood, and their completeness is surprising.

But one conception has been added to Faraday's teaching that of electrolytic or ionic dissociation or ionisation." Although introduced by Clausius in 1857, it lay dormant until it was reintroduced and applied by Arrhenius in 1884, who gave to the hypothesis a quantitative form; but it did not become popular until 1887, when Van't Hoff introduced the conception of osmotic pressure. The successful application of the hypothesis in explanation of the abnormally high results obtained in the case of conducting solutions at once secured for it a very large measure of support. Whatever view may ultimately be taken of the hypothesis—whether it be retained as a permanent addition to our theories or not—its introduction has been eminently fruitful of results, and an already too voluminous literature of the subject has grown up with surprising rapidity. Yet it appears to me that it has been accepted by a particular school—at the head of which stands Ostwald, and who regard and treat all unbelievers as heretics worthy of the stake—not as a mere working hypothesis, but as an absolute creed, without any sufficient attempt having been made to discuss its *general* probability. And the application of Avogadro's axiom to solutions, however successful as affording a mathematical method of discussing results, in principle involves the complete disregard of the essential difference between the liquid and gaseous states, and of the fact that in liquids the molecules are subject to a control which they mutually exercise and which distinguishes the liquid from the gaseous state. Also it must not be forgotten that the arguments made use of apply almost entirely only to weak solutions—to solutions to which a law of simple proportionality may be expected to apply: that, in fact, the region explored is one in which the rate of change is represented practically by a straight line. Lastly, it is applicable only to electrolytes. Personally, I am still entirely unconvinced of the validity of the hypothesis, although no one can be more willing to admit that in so far as *weak* solutions are concerned, a "law" has been discovered which is broadly true *in mathematical form*, however open to question the fundamental premises may be on which it is based. I am satisfied also that the phenomena of chemical change are, as a rule, far more complex in character than is assumed by the advocates of the hypothesis.

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* Series VII, §§ 850, 858, 859; VIII, §§ 869, 918.

If electrolysis, and, therefore, electrolytic conduction be—as I contend and have long contended—conditioned *by a conjoint influence* exercised by the solvent A and the dissolved substance B, there is, I imagine, no reason why other phenomena in which the conjoint influence of A and B comes into account should not be expressible in mathematically similar ways. In extenuation of such heresy, I can only quote Clerk Maxwell's argument that if in a battery a septum be used which diminishes the diffusion, it is probable it will increase in exactly the same ratio the resistance of the element, because electrolytic conduction is a process the mathematical laws of which have the same form as those of diffusion, and whatever interferes with one must interfere equally with the other, the only difference being that diffusion is always going on whilst the current flows only when the battery is in action.

It has always appeared to me that the chief objection to be urged against the ionic dissociation hypothesis is the fact that, of the very large number of compounds known to us, extraordinarily few are electrolytes—not even metallic chlorides generally are conductors, but only a very limited number; and it is particularly remarkable that whilst such inactive substances as lead and silver chlorides, when fused, are among the best conductors known, aluminium chloride—one of the most active compounds with which we are acquainted—is apparently not an electrolyte. Electrolytes are clearly a very limited class, and if we consider the general properties of compounds which conduct more or less readily, whether alone or in solution,[1] and contrast them with compounds which are practically dielectrics, it is impossible to discover any good reason why "ionic disruption" should take place in the case of the one set and not in that of the other. And if, confining our attention to acids, we contrast those which in solution are apparently good conductors with those that are bad conductors, there is again no satisfactory "motive" for so considerable a difference discoverable; for example, taking sulphuric and acetic acids, why should the former suffer ionic dissociation so readily and to so considerable an extent and the latter to so slight an extent? I imagine that it is fair, for this purpose, to regard the acids as modified water, and to assume that the slight tendency of water to undergo ionic dissociation—of which more later on—is enhanced by the association of the water with the oxygenated group, and that whereas sulphuric anhydride has a marked effect, acetic anhydride has a very slight one. Yet this is hardly satisfactory, and would probably involve the conclusion that sulphuric acid should diminish in conductivity as the temperature is raised, as it then dissociates into anhydride and water; the very different behaviour of sulphuric and acetic acids when vaporised, the former but not the latter undergoing dissociation, may be regarded as an indication that a similar change does not take place in the case of acetic acid, and, therefore, it might be supposed that acetic acid would undergo ionic dissociation to a far greater extent than is assumed to be the case as a consequence of the anhydride retaining its influence.

It may possibly be contended, as it has been in the case of water, that compounds generally are conductors to a very slight extent; but as all bad conductors seem to become worse conductors as they are more carefully purified, the burden of proof rests upon those who make such an assertion; and it is not in accord with the fact that very many such compounds are as active as compounds which conduct well, and which are therefore, by hypothesis, more or less fully dissociated. For example, acid chlorides generally act on alcohols generally with very considerable readiness under conditions under which the halhydrides produce but a slight effect.

With regard to water itself, to argue, as Arrhenius, Ostwald, and others have done, from the hydrolytic action of water on the salts of weak acids and bases, that water to a certain but very small extent contains ions, that is, H and OH, is but to beg the question entirely, and a clear case of reasoning in a circle.

The recent redetermination of the electrical conductivity of water by F. Kohlrausch and Heidweiller gives the value $0{\cdot}04\,.\,10^{-10}$ at 18°, instead of $0{\cdot}25\,.\,10^{-10}$ previously arrived at by F. Kohlrausch. These authors have deduced from their results a value for the conductivity of *pure* water, viz., $10^{10}\,.\,\kappa = -0{\cdot}0361$. They calculate that if this conductivity be due to the presence of water ions, a cubic metre of water at 18° would contain 0·08 milligram of dissociated hydrogen ions; and point out that if present only in this excessively minute proportion, there would still be milliards of atoms of hydrogen per cubic millimetre, and neighbouring atoms would be separated by distances of the order of light waves in dimension. These conclusions, however, are based on the acceptance of the view put forward by Arrhenius, that the dissociated ions alone conduct the current—from my point of view, therefore, it is a case of deducing one unknown with the aid of another unknown—of proving one assumption by another assumption, which is admittedly an unsatisfactory proceeding. I venture to think that it is still open to question whether pure water, indeed whether any *pure* substance outside a very limited number perhaps, such as the silver haloïds, &c., be an electrolyte. Minute in the highest degree as the amount of impurity in the water examined by Kohlrausch and Heidweiller must have been, yet even this may have exercised a very considerable effect, and in fact there is clear evidence in the paper that an extremely minute amount of impurity does so act. Moreover, the difference betwen the lowest observed value and the corrected value appears disproportionately small when the reduction of the value previously obtained by Kohlrausch, effected by the removal of what after all must have been a very minute amount of impurity, is considered. The point is one of the utmost importance, and cannot be lightly brushed aside.

The methods made use of in calculating the amount of ionic dissociation of water are apparently all open to the criticism that they are based on eminently hypothetical premises, and it is particularly open to question whether the phenomena from which fundamental values have been deduced have received the proper interpretation. For example, the origin of the E.M.F. developed in liquid couples such as have been studied by Worm Müller, and much later by Nernst, and of the concentration currents of von Helmholtz, is by no means clear. Nernst assumes that in such cases forces acting at the electrode surfaces are entirely eliminated, but, if so, it is not clear why any more than when an acid neutralises an alkali an E.M.F. should be developed, for I imagine that in all such cases the changes take place within closed circuits. In fine, I am inclined to doubt whether polarisation effects can be regarded as eliminated; the enquiry must be included with that into the existence of a true contact difference of potential independent of chemical change. The values deduced by Ostwald are based on the study of couples of the form:—platinum-hydrogen | acid | alkali | hydrogen-platinum, and it is assumed that the E.M.F. developed is due to the formation at the one electrode of water from the hydrogen and the OH ions in the liquid, and at the other of hydrogen from hydrogen ions in the liquid and the hydrogen of the electrode. Unfortunately the description promised of the experiments has not yet been given, and it is therefore difficult to criticise them; it is not impossible, however, that the real cause of the E.M.F. was dissolved oxygen.

Pure liquids do not conduct, according to Kohlrausch, because (as Ostwald has put it, *Brit. Assoc. Report*, 1890, 335) their molecules have no space within which to resolve themselves into ions, and it is therefore not improbable that water would conduct electrolytically—and I presume that Ostwald meant even to imply that it would be a good conductor, as he immediately afterwards spoke of water too containing ions to a certain but very small extent—if we could find a suitable solvent for it. But we never have found a suitable solvent—unless it be hydrogen chloride. The fact that single substances such as the silver haloïds, when liquefied, readily conduct would appear in itself to be a sufficient argument in controversion of Kohlrausch's explanation of the influence of the solvent. Moreover, it is to be supposed that any liquid capable of acting as a solvent should condition electrolysis if the function of the solvent be but to act as a screen.

As a matter of fact, there is good reason to think that among liquids, *water is the only effective solvent that we can use !*

Alcoholic and some other solutions, it is true, conduct more or less well, but it is by no means improbable that when every precaution is taken to deal with highly purified materials, and especially to dehydrate the alcohol as fully as possible, such solutions will be found to be practically destitute of conducting power. This is the more likely now that Perkin has established the incorrectness of the supposition that until recently has always been made that hydrogen chloride, when dissolved in alcohol, acts fairly readily on it (Trans., 1894, 23). The observations made by Coldridge showing that solutions of hydrogen chloride in stannic chloride are but slightly conductive are also significant (*Phil. Mag.*, 1890, **29**, 383).*

If it be assumed that even pure water is to some slight extent dissociated, it is, at least, probable that liquid hydrogen chloride would contain some small proportion of ions prior to admixture with water; and, in point of fact, it is impossible to urge any reason why the one compound should be regarded as more dissociated than the other in the pure state. Yet the "ionists" not only assert that when hydrogen chloride dissolves in water it becomes almost completely separated into its ions, but make the arbitrary assumption that practically it alone is dissociated, the extent to which the water is dissociated being, indeed, diminished by its admixture with hydrogen chloride, according to their view. This question is of fundamental importance as bearing on the validity of the argument on which Ostwald and others have sought to base a method of determining the heat of formation of water from its ions and on the interpretation they have given of the changes attending the neutralisation of acids by alkalis.

I long ago insisted that we have no right to draw any marked distinction between hydrogen chloride on the one hand and water on the other, inasmuch as, in so far as the chemist can test them, they do not differ markedly in stability. I venture to think that no sufficient answer has been made to my objection. To say that analogous compounds such as NCl_3 and PCl_3, or N_2O_5 and P_2O_5, exhibit differences equal to those manifested between HCl and H_2O is incorrect and beside the point—they are vastly different in stability; water and hydrogen chloride are not (compare Ostwald, *Zeit. physikal. Chem.*, 7, 418). So long as it was asserted that water, *per se*, underwent no change, the position was, perhaps, in a measure defensible; but when it is argued that pure water does dissociate into its ions, this advantage is sacrificed; the possibility of a change taking place in pure water being granted, it is no longer justifiable to draw a hard and fast distinction between water and hydrogen chloride. This argument is most materially strengthened by the fact that the majority of compounds are not electrolytes.

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* These observations require to be repeated, taking every possible precaution to exclude moisture.

Although those who uphold the ionic hypothesis regard the solvent as mainly inactive, yet they do not deny that it may exert some influence comparable with that exercised by raising the temperature (compare Ostwald, *Zeit. physikal. Chem.*, 1891, 7, 421; *Lehrbuch*, 2nd ed., 1, 776). But it is impossible to gainsay that it has an altogether extraordinary effect in many cases. For example, in the case of hydrogen chloride, it is only necessary to mix this with nine molecular proportions of water to obtain a solution of maximum conductivity, in which, if we are to believe the ionists, nearly the whole of the dissolved hydrogen chloride is resolved into its ions. It is scarcely conceivable, however, that so small a proportion of water molecules should suffice to practically entirely prevent the reunion of ions which cannot by hypothesis be kept apart in the absence of the solvent; and the conclusion is the more striking if it be remembered that, according to Ostwald, hydrogen silicon fluoride only begins to undergo hydrolysis when present in a solution to the extent of less than 1 per cent., a very large proportion of water being required to prevent the reversal of the interchange $H_2SiF_6 + 2H_2O = SiO_2 + 6HF$—in other words, a compound which is almost generally regarded as a molecular compound is far less readily broken up* than one of the most stable of "atomic compounds!"

Or, taking the case of sulphuric acid, how are we to satisfactorily explain by the ionic dissociation hypothesis the fact established by F. Kohlrausch that the amount of acid required to form a solution of maximum conductivity increases as the temperature rises, from 30·2 at 0° to 35·4 per cent. at 70°? If, however, electrolysis occur within a system of acid and water molecules, as a rise of temperature would promote the occurrence of dissociation in such a system, a larger proportion of acid would be required at higher temperatures to maintain the system of the same average composition.

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* Incidentally it may be asked, how is the formation of hydrogen silicon fluoride from solid silica and hydrogen fluoride to be explained; and how are we to reconcile the fact that action takes place with such extreme readiness when hydrogen fluoride is by hypothesis so slightly dissociated?

In fact, I believe it is impossible to deny that the solvent is intensely active, and that it is no mere screen preventing re-combination of the ions—it is rather to be supposed that the occurrence of electrolysis in a solution of hydrogen chloride, for example, is in some way directly conditioned by the conjoint influence of the solvent and the dissolved substance; that electrolysis is not merely an affair of atoms, of ions, but of complex molecular systems; and, most important of all—*that water, perhaps, is altogether peculiar among solvents as furnishing solutions which can be electrolysed.*

Having thus considered some of the apparent anomalies of the ionic dissociation hypothesis, I may now briefly refer to evidence of its insufficiency in the case of interactions in which substances are concerned which are not electrolytes—a condition which is not fulfilled in the case of a very large number, indeed an overwhelming majority, of carbon compounds. No doubt it may be asserted that, at all events, the agent used is dissociated, and that, consequently, the compound which is attacked is subject to the action of ions just as the zinc is in a voltaic cell. But is this a sufficient explanation? Consider the case of the hydrolysis of sugar—admitting, for the sake of argument, that when this is effected by dilute acid, the ions of the acid and of water either simultaneously or successively attack the sugar molecule; how are we to explain the action of the enzyme invertase? This cannot well be regarded as an electrolyte; and it is not sufficient even to assert that it does, to some slight extent, undergo dissociation into ions—it acts so readily, more readily even than an acid which, by hypothesis, is to a very great extent dissociated, that if at all dissociated it is presumably highly dissociated. The selective action of enzymes on glucosides, &c., is also very remarkable, as acids do not act selectively.

Difficulties such as appear to beset the ionic dissociation hypothesis are not met with in considering the alternative *association* hypothesis, and if this can be shown to be compatible with electrical requirements, it should command more general consideration—in fact, there have been many indications of late that this view is once more coming into prominence. Briefly stated, the hypothesis involves the assumption that complication not simplification precedes most, if not all, chemical changes; that complex molecular systems are first formed from the interacting substances, and that these, on breaking down, suffer rearrangement of the parts—such rearrangement taking place in consequence of elements which were previously separate being brought into one common "sphere of activity" within which it is possible for them to interact. The function of condensing and other agents—of catalysts generally—on this hypothesis is that of collecting into one system the various elements necessary for the occurrence of a particular change. Such systems may be regarded as, and, in fact, would be, closed voltaic circuits or potential circuits requiring only the removal of a resistance to convert them into closed circuits. The action of aluminium chloride, for example, in conditioning the formation of homologues of benzene from the two substances benzene and methyl chloride—both undoubtedly dielectrics, I imagine, which when together alone are entirely without action on each other, may be ascribed to the formation of an unstable compound of both with the metallic chloride. In like manner, it may be supposed that ferric chloride conditions the interaction of bromine and benzene by combining with both, and so bringing them both within each others range in an unstable system. The function of enzymes in promoting hydrolysis, referred to above, on this hypothesis, consists in bringing water into conjunction with the carbohydrate by combining with both. Lastly, if it be assumed that a solution consists of dissociable molecular compounds of solvent and dissolved substance, the occurrence of change on dissolving two substances in a common solvent, as in the case of methyl iodide and silver nitrate in alcohol, may often be conditioned by the solvent acting as "condensing agent" or catalyst.

Professor Fitzgerald, who has carefully considered this hypothesis, if I rightly understand his argument, seems to see no difficulty in applying it to the explanation of electrical phenomena. The modification of Grotthus's hypothesis, which he has suggested, is certainly one which appears to be in entire harmony with chemical experience, and it is so important that the question should be fully discussed, that I will venture to quote his statements almost in their entirety from the *Brit. Assoc. Report*, 1890, 142, where they are too likely to escape general attention.*

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* "Electrolysis has been explained on two different theories by Grotthus and Clausius. As generally received they differ. Grotthus's theory, as generally given, assumes that the molecules in an electrolyte are both polarised and moved by the electric forces within the liquid. This seems so far untenable that it would appear that double the electric force would double both the polarisation and the motion of the molecules, and so should produce four times the electrolysis. The objection, however, assumes that we know the causes resisting the motion, and with proper and not very improbable assumptions as to the resistance to motion depending on it and on the polarisation, a linear relation between current and electromotive force, *i.e.*, obedience to Ohm's law seems possible. A modification of Grotthus's hypothesis in the direction of Clausius's is, however, possible. Suppose that when polarised, the molecules *drew one another apart* at a rate proportional to the

above that the complex systems within which chemical
med to take place would be closed voltaic circuits. It
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change as interdependent phenomena within such systems

sation. This at once makes the relation between electric force and the decom-
tion a linear one, and so satisfies Ohm's law in the case of small currents. It
so so far agrees with Clausius's hypothesis that it explains electrolysis and double decomposition as properties of the same kind. The molecules in a liquid will occasionally be arranged by accident in a proper polarised condition in a closed circuit for drawing one another apart; and if the circuit includes molecules of different kinds, there will result double decomposition. There seem to be very serious difficulties in supposing that uncombined atoms are for any finite time free in the liquid; and the supposition that it is a particular arrangement that is required before exchanges take place, and that with this arrangement exchanges take place of their own accord, seems to explain electrolysis and double decomposition without supposing free atoms to exist within the liquid. . . . .

"There are some other phenomena that have been explained upon the supposition that free atoms are gadding about in a liquid. Such are the lowering of the boiling and freezing points by solutions of salts and their effect on osmotic pressure. If dissociated atoms are going about in a liquid as in a gas, it seems impossible but that they must diffuse at different rates; and that this is not observed seems conclusive against the hypothesis, no matter what else the hypothesis may explain. Consider solution simply. Why does chloride of sodium dissolve in water? There must be some strong affinity between the two of a chemical or semi-chemical nature to break up the cohesion of the crystal; and it seems reasonable to assume that this same affinity keeps the molecules of NaCl moving about among the water molecules so that they diffuse about. Now if the forces drawing them about be independent of the nature of the molecule, most of the phenomena explained by gaseous laws are explained. Pressure of a gas depends, at any temperature, on the number of molecules and not on their kind. This is Avogadro's law, by which molecular weights are calculated; and if the forces drawing a molecule about in a liquid are independent of the kind of molecule, the very same law of pressure would hold, the pressure forwards of molecules of different kinds would depend on their number only, and in the same way as Avogadro's law would enable molecular weights to be calculated. In this connection it is well to state that some bodies may be much better able to produce pressure than others, because of their being more easily polarised, *i.e.*, turned into an effective direction. A molecule which could be easily turned into an effective direction would be about twice as effective as a molecule which went about in a higgledy-piggledy way; and one would consequently expect electrolytes to produce more, nearly double, the osmotic pressure that others did. As to the changes of boiling and freezing points, they seem explicable by exactly the same hypothesis. The reduction of vapour pressure by molecular affinity of dissolved salt would depend only on the number of molecules of salt if all salts have the same molecular affinity for water; and the same would apply to the change in freezing point. Hence all these phenomena are explained without assuming free atoms, and they are all explained by what can hardly avoid being a *vera causa*, namely, whatever affinities they are that cause solution, which latter is an unexplained phenomenon on the dissociation hypothesis. That it is reasonable to think that the forces keeping the molecules of salt moving about in the water are independent of the nature of the salt, appears from various considerawill frequently evade detection, as more often than not we have to do with circuits which cannot be explored; and on this account also our power of availing ourselves of the energy of chemical change is strictly limited. Probably no discovery could be made which would be of greater technical importance than the discovery of a method of burning fuel electrically, *i.e.*, so as to produce electricity instead of heat. Hydrogen may be burnt electrically in the manner discovered by Grove, apparently because it is possible by means of platinum to connect both hydrogen and oxygen in circuit with an electrolyte such as diluted sulphuric acid; but we have not yet succeeded in discovering a method of "plating" a conductor with carbonic oxide which would enable us to arrange it in a circuit with oxygen. If this could be done, probably the problem would be soon solved. In the case of solid fuel the problem presents other difficulties, especially that arising from the want of suitable electrolytes: thus, although heated lead oxide is readily reduced by carbon, it does not behave as an electrolyte when the attempt is made to burn carbon electrically by means of it, the action being purely local. In like manner we have to discover a means of converting nitrogen into either ammonia or a nitrate comparable with that which apparently enables the papilionaceous plant or associated bacteroid to assimilate nitrogen from the atmosphere.

Having broadly laid down the principle that chemical changes consist in the exchange of ions, and therefore take place exclusively between ions, the "ionists" may be presumed to accept the view that chemical and electrolytic changes generally are synonymous operations. This being the case, it is remarkable how little has been done by way of applying the hypothesis except as a means of correcting values obtained in working with solutions which behave as electrolytes. The expansion and application of Faraday's conceptions to the explanation of chemical change generally appears indeed to have been retarded rather than advanced by the assertions formulated by the advocates of ionisation as a precedent cause of chemical change; indeed Faraday's writings appear to have received no notice from the school. No attempt has been made to differentiate electrolytes from dielectrics by explaining either the essential peculiarities of either class or the co-ordination of composition, *i.e.*, structure, and function; or to explain the extreme readiness with which dielectrics are in many cases acted on; or to define the conditions under which

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tions. In the first place, these forces are in all probability due to the residual affinities of the non-metallic elements. These same forces are probably the cause of crystallisation. These are old suggestions. That these residual affinities should be nearly the same for different combinations does not seem at all unlikely . . ."

chemical change will occur; or to explain the readiness with which a minute amount of "impurity" will often condition change.

Whatever hypothesis be adopted, the determination of the essential qualities of an electrolyte—a correct answer to the question: What is an electrolyte?—is of fundamental importance. The electricians would say it is a substance which, whilst conducting, undergoes decomposition, which is a purely practical definition. The "ionists" say that it is a substance in a state of ionic dissociation; but theirs is a dissociation of a most mysterious kind—confined to a very limited number of substances—affecting members of the same group in a most arbitrary manner, as whilst some respond, others do not, to the call to ionise on entering into solution—in no way to be co-ordinated with their relative stability as determined by any ordinary chemical method—and conditioned by the agency of a solvent which, though by hypothesis a mere screen, yet exercises a most potent influence, as solvents generally besides this one have little if any action. I discussed the question tentatively at Aberdeen, but did not arrive at any satisfactory conclusion as regards compounds which *per se* act as electrolytes. Facts have since come to light which make me more hopeful. In the case of the metallic protochlorides, so many of which are electrolytes, whilst the corresponding perchlorides are not, electrolysis involves the chloride acting both as electrolyte and "chlorine depolariser," and it is conceivable that the occurrence of decomposition is dependent on, and in a measure conditioned by, the depolarisation—in other words, that separate molecules are conjointly influenced by the electromotive force, and that while under it the one molecule promotes the decomposition of the other. The readiness with which the silver and lead haloïds undergo electrolysis may be explained in a similar manner, if it be assumed that they are capable of exercising at least a temporary affinity for halogens. It is remarkable that the elements from which electrolysable haloïds are derived occur closely together in the periodic system, and it may be said within the section of the alkali metals. As the alkali metals form tri-iodides, and similar compounds have been obtained from silver haloids, as well as tetrahaloïd compounds of lead, there is reason to believe that the power of attracting halogens here postulated is actually existent, especially at high temperatures, when the fundamental molecules may be supposed to be more or less free from mutual control, and more likely, therefore, to form compounds with other elements.

From this point of view, the behaviour of silver haloïds and of other substances which act as simple electrolytes is strictly comparable with that of composite electrolytes, as I have termed conducting mixtures of dielectrics; and if such a view could be accepted, the phenomenon of electrolysis would appear to be strictly comparable with those of chemical change—both would occur within complex molecular systems. The behaviour of aqueous solutions on electrolysis may conceivably be more analogous to that of haloïds than is commonly supposed, if it should turn out, for example, that, in the case of solutions of sulphuric acid in water, the first products of electrolysis are, as I have tentatively argued (compare Proceedings, 1893, 190), hydrogen and *persulphuric acid.* As I will show later on, it would not be difficult to apply a similar hypothesis to other acids and generally to aqueous solutions—especially if water be the *significant* substance in all these changes.

In discussing this, it is necessary to consider the acids themselves, as the suggestion here made in a measure involves the conception that acids such as sulphuric acid are hydrates, not hydroxides. Without attempting to discuss this matter in detail, I may say that, in my opinion, there is no evidence which in any way obliges us to regard sulphuric acid as $SO_2(OH)_2$; on the contrary, all the arguments are equally compatible with the assumption that it is a compound such as may be represented by the formula $SO_3{\cdot}OH_2$, in which the radicles SO_3 and OH_2 are still preserved. There is no reason why such a view should not be extended to all "inorganic" acids, and if it be assumed that solutions of the halhydrides contain hydrates, the behaviour of such solutions as acids is strictly comparable with that of acids generally. Organic acids are peculiar in so many ways that they may well also be peculiar in their constitution and different from those derived from elementary oxides.

If sulphuric acid be a hydrate, viz., $SO_3{\cdot}OH_2$, persulphuric acid is probably $SO_3{\cdot}O_2H_2$,* and the formation of the latter during electrolysis as the primary product would, in a sense, involve the oxidation of water, so that the change would be similar in form to that which I have supposed to occur when a silver haloïd is electrolysed. By thus extending the view that electrolysis is the outcome of the combined action of the electromotive force and of some effect which the one set of molecules exerts upon the other set while both are under the influence of the electromotive force, a clearer conception is gained of the possible nature of the effect which the one set of molecules exercises on the other set. The peculiar value of water as a solvent is also in a measure explained.

As regards the differences observed between acids, I have elsewhere pointed out in a note on the formation of salts (*Chem. Soc. Proc.*, 1891, p. 118), that "It may be supposed that in all cases the acid and the base in the first instance combine, and that the salt is formed by subsequent interactions within the molecule. In like manner, acids form dissociable compounds with water, and it is by the occurrence of change within such systems under the influence of an electromotive force that electrolysis is effected. In those cases in which the compound is highly unstable and prone to dissociate, the opportunity for change to take place within the system is but slight, and consequently the acid is a weak one and its solution of relatively low conducting power."

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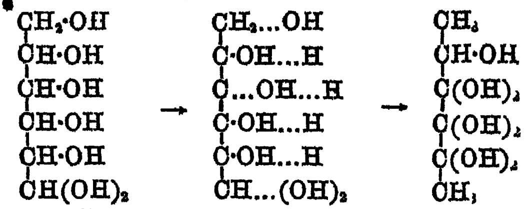
* Berthelot has actually obtained a persulphate from sulphuric anhydride and a peroxide.

The argument here used would apply equally to alkalis and salts, although it may be doubted whether dissolved salts as such promote electrolysis: it is not improbable that they are more or less hydrolysed, and that the products condition electrolysis; on this assumption, the conductivities of salt solutions afford a measure of the extent to which hydrolysis has taken place in them.

Experience shows that action at once necessarily takes place so soon as a conducting circuit is established, provided that the sum of the changes be exothermic—thus, copper readily dissolves in cold dilute sulphuric acid if coupled with platinum in nitric acid, or in presence of oxygen, although the heat of dissolution of copper in sulphuric acid is negative. This principle is one of extraordinary importance, and I desire to draw attention to one illustration of its application which I believe to be of consequence. It is well-known that Baeyer in 1870 pointed out that the resolution of glucose during fermentation into alcohol and carbon dioxide, and, indeed, the phenomena of fermentation generally, may be accounted for by the assumption that translocation of hydrogen and oxygen atoms is induced through the alternate separation of the elements of water and their addition in different order, changes which would involve the accumulation of oxygen atoms at certain parts of the molecule, thus constituting points of weakness where disruption of the molecule would inevitably occur. This is shown in the following formulæ, in the second of which the separating elements are indicated by dots.



$$\begin{array}{ccccc} CH_2{\cdot}OH & & CH_2 \ldots OH & & CH_3 \\ | & & | & & | \\ CH{\cdot}OH & & C{\cdot}OH \ldots H & & CH{\cdot}OH \\ | & & | & & | \\ CH{\cdot}OH & \rightarrow & C \ldots OH \ldots H & \rightarrow & C(OH)_2 \\ | & & | & & | \\ CH{\cdot}OH & & C{\cdot}OH \ldots H & & C(OH)_2 \\ | & & | & & | \\ CH{\cdot}OH & & C{\cdot}OH \ldots H & & C(OH)_2 \\ | & & | & & | \\ CH(OH)_2 & & CH \ldots (OH)_2 & & CH_3 \\ \text{I.} & & \text{II.} & & \text{III.} \end{array}$$

It will be seen that in the product of rehydration (III), the terminal groups are fully reduced, whilst there has been an accumulation of OH groups in other parts of the system. In a molecule so constituted, changes might then set in similar to those involved in the resolution of oxalic acid into carbon dioxide and formic acid.

The conception is one of remarkable beauty, and undoubtedly a sufficient explanation, as changes precisely similar to those attending fermentation may be effected by simple hydrolysis: thus glucose may be converted into lactic acid by heating it with alkali; and on boiling fructose with muriatic acid an acid is formed, *i.e.*, lævulinic acid, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$, the production of which clearly involves a reduction of some of the $CH_2{\cdot}OH$ and $CH{\cdot}OH$ groups, and oxidation of others, in the manner pictured by Baeyer. The only difficulty is to account for the occurrence of such changes under the conditions prevailing during fermentation, and here Baeyer has left the problem unsolved.

I have already drawn attention to the manner in which, perhaps, enzymes promote the hydrolysis of glucosidic compounds. A slight extension of the hypothesis appears to be all that is required to afford an explanation of the changes attending fermentation. Such changes are known to occur entirely within the cell, and are, presumably, functions of the protoplasm—in other words, they probably occur within very complex molecular systems of extreme instability: perhaps under the influence of, in contact with, the very same hydrolyst (enzyme) which, when separated from the cell, is so active in promoting the hydrolysis of cane sugar; or, if not, of substances of a similar nature. On inspecting Baeyer's formulæ, it will be noticed that during rehydration the elements of the water molecule become added on to non-contiguous carbon-atoms, and this is not improbably frequently a special feature of such changes. Supposing that the protoplasmic hydrolyst were to condition the formation of a conducting circuit in which any two of the carbon systems ($CH_2{\cdot}OH$, $CH{\cdot}OH$ or COH) of the glucose molecule and water molecules were included, if the total hydrolytic change which could take place in such a circuit were exothermic, even if the change affecting the one group involved an expenditure of energy, water would be electrolysed, and its hydrogen would effect the withdrawal of OH from the one group and its displacement by hydrogen, while oxygen would be added to the other group, it may be directly, or in consequence of the displacement of H by OH. The different effects produced by different organisms, on this hypothesis, would be the consequence of the hydrolysis affecting different systems. As most, if not all, fermentable compounds are asymmetric, and the enzymes are undoubtedly also asymmetric bodies, the direction of attack would depend on the character of the asymmetry of both hydrolyte and hydrolyst (for nomenclature see Trans., 1890, 528), and only compatible hydrolysts, *i.e.*, those compatible with the hydrolyte, would condition hydrolysis and fermentation. I venture to think that the hypothesis here put forward* not only affords a sufficient explanation of the occurrence of change in the manner suggested by Baeyer, but is also of value as indicating a process by which the "energy" which is in defect in one part of a complex molecule may be supplied from another part, a point of some importance, as E. Fischer's marvellous researches on the carbohydrates and similar compounds clearly prove that the several groups of which the carbon-atoms are centres in such molecules are practically independent systems which require to be individually influenced.

Considerations such as these may obviously be applied to all cases of chemical change in which complex asymmetric compounds are concerned, and are possibly of wide application in explanation of the chemistry of vital processes, including those of disease and death.

The introduction of new elements into the circuits within which normal changes occur, even if these were to remain conducting, would necessarily condition some variation in the rate, if not in the character, of the change, and even neutral substances would interfere and affect the rate of dissociation (hydration), for it is probable that the systems under consideration are eminently unstable. The interposition of non-conductors would cause "death" within the circuit affected, and hence indirectly in others. The effects produced by alcohol are, perhaps, explicable from this point of view.

In the case of vital processes, it may be pointed out that one great distinction which apparently may be drawn between actions taking place under "vital" conditions and those effected in the laboratory arises from the circumstance that in the former case a number of changes of distinct types may more often take place, if not simultaneously, at least in rapid succession, affecting different and it may be distant parts of a molecule. It would seem that while included within the protoplasmic molecule, in some cases also protection is afforded to that part of the molecule which if free would be the first to suffer, as in the case of the oxidation of glucose to glucuronic acid, for example, the attack being consequently directed into unusual channels; and that in others, molecules are brought into association and caused to interact which under ordinary conditions would fail to affect each other.

Whatever the nature of "protoplasmic" molecules, they must be of extreme complexity and, consequently, they must present very many active regions to which other groups may become attached and within which therefore circuits can be established: hence the marvellous power of protoplasm of conditioning a great variety of changes; and it is doubtless the marvellous complexity of the albuminoids which renders such diversity of type possible in both the animal and vegetable kingdoms. Protoplasmic molecules may indeed be likened to a huge modern manufactory within which a great variety of operations are being carried on—almost all, in fact, that are necessary for the production in its finished state from raw materials of the particular article manufactured; many of the operations go on independently, others consecutively and dependently: yet all are carried out under one guiding impulse, within one sphere of action.

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* A verbal statement of the hypothesis was made in the course of a discussion in which sections B and D took part at the Bath meeting of the British Association in 1888, and I also spoke of it in the course of lectures delivered at the Pharmaceutical Society in 1892.

It can scarcely be doubted that the truth of Faraday's doctrine of the unity of chemical and electrolytic change will ere long be generally recognised now that it has been shown in so many cases that interaction does not occur between *two* (pure) substances.

The essential moment conditioning the occurrence of chemical change, according to the view of which I am an advocate, is the formation of a conducting system in which electrolysis can occur, and within which, as already said, change will necessarily take place so soon as the system is established, if exothermic change be possible under the conditions—as in the case of any voltaic cell. Substitutions on this hypothesis are but secondary results consequent on additions.

Much has been done of late to discover that water plays an all-important part in determining many chemical changes, but the nature of the influence which it exerts has been little considered, and I am alone, I believe, in pointing out that mere moisture should be insufficient to condition change in many cases—in the formation of water, for example, from hydrogen and oxygen, the interaction of nitric oxide and oxygen, or the action of chlorine on metals, &c., as in such cases there would not be an electrolyte present. On th other hand, it would presumably suffice to determine the interactio of ammonia and hydrogen chloride, for example, as the latter an water together form an electrolyte. I believe this to be the criterio by which the efficiency of water *per se* may be judged of: in othe words, that it will *per se* condition the occurrence of an interactio between two substances only if it be capable of forming a composi electrolyte with at least one of them; in all other cases somethi besides water must be present which will render the water condu ing by forming with it a composite electrolyte. The number of su substances is, as already pointed out, comparatively limited.

In further illustration of this argument, the rusting of iron may referred to, as notwithstanding its importance and the amoun discussion it has given rise to, the exact nature of the change i no means determined. According to Crum Brown (*Journ. Iron and Steel Institute*, 1888, 2, 129), liquid water, oxygen and carbon dioxide are the essential elements concerned in the formation of rust. But it may well be doubted if a solution of carbon dioxide in pure water be an electrolyte, in which case perhaps the carbon dioxide initially but serves to promote the formation of acid from a trace of some salt which happens to be present, and the primary product derived from the iron is the corresponding iron salt; this last, however, being even more amenable to attack by carbon dioxide than the salt originally present, the acid is continually regenerated. On this view, it is easy to understand the protection afforded by an alkali. I have on more than one occasion urged that probably it is always necessary that liquid water systems should be formed if change is to occur, at least in the case of changes taking place under ordinary conditions, *i.e.*, at ordinary temperatures. Apparently it is only at high temperatures or under the influence of an electric discharge, that this condition need not be secured, and in such cases it may be supposed that the conditions are such as to favour the momentary formation of what are practically liquid systems in the atmosphere within which the change occurs. It is not improbable that the influence which surfaces often exercise in promoting gaseous changes may at least in some part be due to the increased opportunity they afford for the formation of liquid systems to take place.

The absolute function which the (composite) electrolyte fulfils in such systems is obscure at present, as it is but stating a fact to say that the presence of a conductor is essential in order that a current may flow: it would seem not improbable that it in some way constitutes a mechanism whereby the discharge or degradation of the energy expended in the change is effected. The question is one of great interest and importance, especially when viewed in connection with the inquiry into the nature of valency and with the fact that an action impossible within an endothermic system at once takes place when an element (a depolariser) is introduced which constitutes the system one within which as a whole endothermic change can occur.

H. B. Dixon's observations on the combustion of carbonic oxide, as well as those of Victor Meyer and his co-workers on the formation of water, and also those of Pringsheim, followed by those of Victor Meyer and Bodenstein, on the formation of hydrogen chloride, all bring into prominence the fact that the occurrence of change in gases is dependent on conditions which are essentially of the same order as those obtaining in the case of liquids. Professor J. J. Thomson's observations on the discharge of electricity through gases (*Phil. Mag.*, 1893, 36, 313) apparently prove that what is true of chemical change is equally true of the electrical discharges which can be produced in rarefied gases—that the phenomena in both cases, in fact, are electrolytic manifestations, and that discharge could not take place in a pure gas. It appears to me unnecessary to assume that such changes are dependent on the occurrence of atomic dissociation of the molecules of the interacting substances prior to the formation of the molecules of the substances which are the ultimate products; indeed, the observations referred to may almost be regarded as proof that such is not the case No more striking evidence that the occurrence of a discharge in a gas is dependent on the presence of a something besides the gas—on the formation of a complex conducting system—could be given than is afforded by the beautiful experiment exhibited by Dewar at the Royal Institution, showing that the discharge at once ceases in one of Crookes's phosphorescent tubes on cooling with liquid oxygen. Such treatment cannot be supposed to cause the condensation of the residual air, but may well condition the deposition of the traces of vapour (? of conducting water) present in the gas, thereby destroying the systems within which conduction can alone occur.*

It may be here pointed out that this argument is perhaps also at least partially applicable in explanation of the erratic behaviour of the discharge in vacuum tubes. If the discharge occur within a complex system, it may well be that certain conditions will favour the formation of a conducting system including one, and others of a system including another, of several substances present in a tube—such an explanation, for example, would account for the fact that the mercury spectrum is only sometimes seen in tubes connected with a mercury pump. And having regard to the fact that a gas may exhibit several spectra, it may be that the spectrum of a given substance varies more or less according as it is included in one or other of several conducting systems.

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* It is noteworthy that J. J. Thomson himself draws the conclusion from his experiments that the discharge through a gas does not consist in tearing the atoms of a single molecule apart, but rather in tearing atoms from off complex aggregates of molecules. I may here point out, with reference to his observation that a much higher potential difference is required to start a discharge in a highly dried gas than is required to maintain the discharge when once it has taken place, that if a trace of air were present a trace of nitric acid would be formed, which might render the minute amount of moisture present conducting; during rest this would be attracted to the walls of the tube, and therefore it would be at first difficult again to start the discharge, as, indeed, he found to be the case.

The proof given by H. B. Baker that dried hydrogen chloride and ammonia are incapable of interacting seems also to be a strong argument against the conclusion that combination takes place between dissociated atoms. The admixture of the two gases should have, as consequence, the dissociation at least of the haloïd, if the states of liquid and gaseous solution be directly comparable, as it is asserted they are.

While referring to ammonium compounds, it may also be pointed out that the fact that the alkyl-ammonium haloïds, such as NMe_4I, &c., are not acted on by caustic potash, but readily by silver hydroxide, is difficult to explain from the ionic dissociation point of view. *Ex hypothesi*, the haloïd and silver hydroxide are both to be regarded as dissociated, as they interact; but potash is very largely dissociated, much more, in fact, than the analogous silver hydroxide—why, then, is it inactive?

If the occurrence of chemical change be dependent on the formation of liquid or quasi-liquid systems, the reduction of temperature sufficiently to produce solidification should prevent change. This is probably the explanation of observations such as have been made by Dewar and Pictet. There is probably no more effective method of drying, if drying be defined as the removal of liquid water, than that afforded by cooling to the very low temperatures obtained with the aid of liquid oxygen. In like manner, I am inclined to doubt whether any photographic action be possible at very low temperatures, and would attribute the slight effect observed by Dewar to the action of the phosphorescent light emitted by the plate itself on the sensitive film after the temperature has risen sufficiently for the water within the film again to become liquid. I have long been convinced that photographic phenomena and procedure can and should be treated from the electrolytic point of view (*Camera Club Journal*, 1892, 61, 124; 1893, 48, 71).

We are but beginning to recognise that what is true of ordinary interchanges, *i.e.*, that the change takes place within a complex conducting system, must be equally true of changes of the converse order, so-called decompositions, including dissociation phenomena generally. Among the chief experimental contributions to our knowledge of this subject, we may reckon first and foremost the classical work of Grove on the decomposition of water at high temperatures, and the observations of Deville, as well as those of Victor Meyer and Langer, showing that the decomposition of carbon dioxide takes place in porcelain at a temperature several hundred degrees below that at which it occurs in platinum vessels. Perhaps Frederick Siemens, more than any one, has dwelt on the influence of conditions other than those of mere temperature on the stability of substances at high temperatures.

It must always appear paradoxical that water should undergo decomposition at a temperature which necessarily must be below that which can be developed in its formation by combustion from hydrogen and oxygen; or, assuming that the effect is primarily of an electrical character, that it should be decomposed by an electromotive force lower than that which can be developed by the interaction of the elements into which it is resolved.

The problem is akin to that involved in the electrolysis of water, which can be effected by electromotive forces much smaller than about 1·4 volts, the value calculated from the known heat of formation of water.

Two explanations are possible—one involving the assumption of dissociation, the other of an available external source of energy; it is needless to say that the former has long been the popular view. Reference has already been made to current views on the dissociation of water, and the question raised whether we are justified in concluding that water under ordinary conditions is dissociated, even to a very slight extent. But, whatever the ultimate conclusion, even if pure water be undissociated and an absolute dielectric, it may well be that in the case of a conducting mixture we are dealing with systems which, although free from any elements of dissociation, may yet be prone to undergo internal changes much after the manner of those pictured by Williamson in his celebrated essay on etherification (*J. Chem. Soc*, 1851, 4, 110), changes which, as Fitzgerald has pointed out, would in effect be of the same order as those postulated by the modern school of dissociationists. On the other hand, it is not impossible that our conclusions are all based on observations made either with polarised electrodes or with media which have been to some extent impure.

In the experiment devised by Helmholtz and described in his Faraday lecture, the attempt was made, by means of an additional electrode of palladium which could be charged with hydrogen, to remove all traces of dissolved oxygen, and this object is supposed to have been effected; but I venture to doubt the possibility of securing complete depolarisation in such a manner.

With regard to its behaviour at high temperatures, if pure water be to some slight extent dissociated, even under ordinary conditions, as is suggested, it may fairly be expected that it would undergo further dissociation, to a greater extent and more readily than appears to be the case, as the temperature is raised; the important experiments made by V. Meyer and Langer on the behaviour of various gases at very high temperatures apparently also lend no support to this view. The dissociation of water takes place more particularly in contact with heated platinum—copper, although readily oxidised, appears to have no specific influence in promoting its decomposition. Platinum, however, occludes both hydrogen and oxygen and may be supposed to be always charged with one or other of these gases—so that if the decomposition of water at high temperatures by platinum take place within a circuit including one or other of these gases, the electromotive force required to produce the change will be lower than that developed in the formation of water owing to the operation of a back electromotive force. It may be that heated copper does not decompose water, both because it does not polarise as does platinum, and perhaps, also, because the heat of formation of its oxide is lower than that of water under all conditions.

H. B. Baker's observations on the influence of moisture on the decomposition of ammonium chloride by heat (Trans., 1894, 65, 615) are of great importance as the first of their kind, and must serve to direct attention to the value of further experiments of a similar character. It does not appear to me that we are yet justified in assuming that if dry such a substance would not decompose if heated; should we not perhaps rather consider that it would decompose somewhat suddenly when a sufficiently high temperature was reached—when the temperature was, in fact, a trifle higher than that corresponding to its heat of formation? The presence of moisture would promote decomposition because it is capable of interacting exothermically with one of the products, viz., hydrogen chloride. As change is influenced in both directions by moisture, the rate at which it would proceed in a case like that of ammonium chloride would, therefore, depend on the amount of moisture present; if the amount were very small the pressure of dissociation would be attained only after the lapse of a considerable interval of time. The interesting account recently given by Rose (Trans., 1895, 61, 893) of his observations on the influence of moisture on the pressure of dissociation of gold chloride—the first of their kind made to test this view I think, clearly appears to afford confirmation of the correctness of this conclusion. With reference to this question, it may be here suggested that the occurrence of but slight decomposition when calcium carbonate is strongly heated in almost closed vessels may be due not only to the fact that under such conditions the maximum opportunity is given for recombination, but also to the almost complete exclusion of moisture under such conditions. The practice of burning chalk wet is calculated to favour the maintenance of the "back electromotive force" developed in the interaction of lime and water to the utmost possible extent, and thus to hasten the rate of change; in other words, the acceleration is not the outcome of the removal of the gaseous products of change alone. Similar considerations apply to the incomplete *per saltum* combustion of gaseous mixtures at high temperatures.

It is an interesting question whether compounds such as potassium chlorate, which decompose exothermically, will be affected by the presence of moisture or substances exercising equivalent effects; and this inquiry is clearly of special importance in connection with that into the stability of explosives. Baker's experiments have afforded negative results, but the subject is deserving of much closer experimental study. In such cases we are dealing with closed systems in a measure comparable with a charged Leyden jar, in which there are parts capable of interacting kept asunder by a non-conductor. The question is whether change be induced by communication being set up between these distant parts by the interposition of an external conductor, or, in other words, the completion of a circuit; or whether it be the outcome of a disturbance similar to that which would have the effect in the case of a Leyden jar of smashing aside the dielectric at some point, and consequently of bringing into contact the two coatings previously kept apart. The manner in which the decomposition of potassium chlorate is promoted by the presence of various substances might be regarded as evidence in favour of the former view were it not that anything which would give rise to changes developing a back electromotive force would at once alter and, of course, increase the rate of change; and such actions are clearly not impossible in the case in question. It would be a matter of great interest to closely study the behaviour of some of the complex carboxylic acids which lose carbon dioxide when heated, or of the keto-acids from which carbon monoxide is evolved, with the object of ascertaining whether the rate of change is in any way dependent on the amount of impurity present—whether, in fact, such compounds would prove to be the more stable the greater the care taken in their purification, including dehydration under purification; but it is not to be expected that positive results will be attained in such cases until the approach to purity becomes very close. In the case of single substances undergoing rearrangement of parts, it is not unlikely that "residual affinity" may come into play as much as it does in the case of ordinary interactions, and, therefore, that such decompositions will equally depend on the realisation of particular conditions; in other words, that the stability of compounds ordinarily reckoned very unstable may be very considerable in the pure state.

The instability of liquid ozone, to which attention has been drawn by Dewar and Liveing's observations, for example, may not be an intrinsic property of ozone in the liquid state, but may be conditioned by the circumstance that being liquid it is more readily brought into circuit or coupled up with impurities which happen to be present, so that opportunity is given for change to set in. The decomposition of liquid ozone would seem, in fact, to be comparable with that of a liquid system of sulphur dioxide, oxygen and water, in which change occurs somewhat readily, although a gaseous mixture of the same substance is stable, according to H. B. Dixon.

The argument that changes generally all occur within compound circuits may, perhaps, even be extended to complex molecules undergoing change locally, and, indeed, such a step is but an application of the principle already made use of in explanation of fermentation; thus, it is now well known, from E. Fischer's observations, that when certain salts of gluconic and similar acids are heated they are converted into isomeric acids in consequence of a change in orientation being brought about which is purely local, affecting, as it does, only the single asymmetric carbon atom to which the carboxyl group of the acid is attached: the change is, therefore, clearly one which takes place within a local circuit, and apparently requires for its occurrence the establishment of certain special conditions. Lastly, it may be pointed out that cases of so-called tautomeric, or, as I prefer to call them, isodynamic, change, would be easily explicable in terms of the theory here advanced, without in any way regarding them as spontaneous manifestations of inherent intramolecular activities.

I would here direct attention to the interesting discussion which has taken place within recent years as to the origin of flame spectra, as to whether such spectra are heat effects pure and simple or conditioned by the occurrence of some form of chemical change (compare Smithells, *Phil. Mag.*, 1894, [5], **37**, 245, where reference is made to the work of several observers bearing on this subject), questions on which the last word is clearly far from being said. This, moreover, is but one aspect of the wider and deeply interesting problem as to the nature of the changes occurring in flames generally and of those which give rise to luminosity. It has long been taught that the hydrogen is the more combustible element of hydrocarbons, and, doubtless, this doctrine has been too dogmatically and exclusively taught; but the more modern opposite view, which is tending to become fashionable, is probably based on an equally narrow interpretation of the phenomena, which, it can scarcely be doubted, are of a very complex character and likely to defy our powers of analysis for some time to come. Personally, I see no absurdity in the idea that the hydrogen is first burnt and carbon liberated, and the water subsequently unburnt by the carbon; but I prefer to represent such combustions as occurring within systems comprising at least oxygen, hydrocarbon and water, and the products as being water, carbon monoxide and hydrogen. In such a case, I think it would be incorrect to speak of either constituent as the more combustible; the nature of the change must depend on the nature of the circuit within which the change occurs, and this may well vary with the conditions.

I have always felt attracted to the views of the origin of luminosity in flames put forward by Frankland so far back as 1867, in a remarkable course of lectures delivered at the Royal Institution, which were fully reported at the time in the *Journal of Gas Lighting*, and it has seemed to me that the theory has received far less attention than should have been accorded to it. Interest should be revived in the subject by the recent observations of V. B. Lewes (*Proc. Roy. Soc.*, 1895, **57**, 450) on the decomposition of acetylene at high temperatures, which have led him to suggest that this compound plays the chief part in promoting luminosity in hydrocarbon flames, and that the heat liberated during its decomposition endows the carbon particles produced from it with an incandescence far higher than corresponds to the temperature of the flame. It appears to me that while accepting this as a partial explanation, it is unnecessary to suppose that luminosity is consequent on the production of presumably solid carbon particles; the conversion of acetylene, or other hydrocarbons, at high temperatures into hydrogen and carbon, although a decomposition in the ordinary sense of the term, is doubtless a change involving the interaction of several molecules, and the consequent formation of carbon molecules of a high order of complexity together with hydrogen molecules; and it is exothermic because the energy liberated in the combination of the carbon atoms among themselves, and also of the hydrogen atoms, is far in excess of that absorbed in the decomposition of the hydrocarbon molecules. The initial luminance may therefore well be that of the molecules at the moment of formation prior to condensation, although the continued incandescence of the carbon molecules after their reduction to the solid state probably contributes largely to maintain luminosity, giving to hydrocarbon flames their special value, perhaps. But this is to explain the phenomena in terms of Frankland's theory, as I understand it, and as appears to be necessary in order to explain the luminous appearance of a hydrogen-oxygen flame burning under pressure, and other cases in which the products of combustion are gaseous.

Of the many directions in which the introduction of electrical conceptions into chemistry promises to be of service, the determination of the "electromotive efficiency" of chemical change appears to be one of the most important.

Braun in Germany, and in this country our late distinguished Fellow, Alder Wright, whose loss we so much deplore, have devoted much attention to the determination of "chemical affinity" in terms of electromotive force, following the method first adopted by Wm. Thomson (now Lord Kelvin), and successfully applied by him to the Daniell cell. Thomson's calculations involved the assumption that the energy of chemical change becomes wholly converted into electrical energy, but the comparisons which have been since made *seem* to show that in cells other than the Daniell this is rarely, if ever, the case. Holmholtz and others, in fact, have proposed to draw a distinction a free and bound energy, the latter being that portion of the energy of the system which is not convertible into electrical gy but becomes frittered down into heat in chemical changes. has always seemed to me that most physicists who have discussed hose matters have had far too little feeling as regards the nature of chemical changes, and that the conclusions have been too often based on *a priori* considerations. Obviously, it is necessary to know the precise character of the changes going on under particular conditions in any cell before the attempt can be made to ascertain whether the electromotive force developed is the precise equivalent of their "chemical energy." Our knowledge as to what goes on in solutions is so vague, however, that at present we can never assert that we know precisely what is happening in a particular system. As Herroun has pointed out in an important paper on "The Divergence of Electromotive Forces from Thermochemical Data" (*Phil. Mag.*, March, 1889, 209), there is reason to believe that in the case of a number of metals, silver and mercury, for example, it is probably altogether wrong to base calculations on the assumption that the heat of formation of a hydrated salt, or of the salt in a solution of the concentration of that which is ultimately formed in the cell in which the metal is dissolved, is the heat of formation to be made use of in the calculation of electromotive force; we must, in many cases, rather assume that the anhydrous salt is alone formed in the circuit. In like manner, Robertson and I have contended (*Roy. Soc. Proc.*, 1891, 50, 108) that in the lead-sulphuric acid-lead peroxide cell the active acid is not that actually filled in, but a lower hydrate or the anhydrous acid; in this manner it is possible to account for the cooling observed during the discharge of an "accumulator," as the separation of molecules of the acid from a solution (by dissociation) would, of course, involve cooling.

If, as Faraday has said, the forces termed chemical affinity and electricity are one and the same, there does not seem to be any reason why there should not be an integral conversion of the energy of chemical change, nor any necessarily valid objection to the view that an explanation of the discrepancies which have been observed is to be sought for in phenomena that prevent an integral "conversion" from being realised. Meanwhile, the determination of electromotive force may be of great service as enabling us to discriminate between a number of conceivable modes in which change may occur in a given case. Thus it is clear, for example, that whereas a metal like zinc is dissolved by, say, sulphuric acid in a circuit of which the hydrated, not the anhydrous, acid forms a part, metals like silver, mercury, lead and even nickel (compare Herroun, *loc. cit.*, p. 226) require to be coupled with, it may be, the anhydrous acid, but, in any case, with one which is less hydrated than that which is active in the case of zinc; the anhydrous salts formed in such cases apparently undergo hydration outside the circuit of electrolytic change, and their hydration only affects the temperature of the cell, so that the phenomena are comparable with those which attend local action in a cell in which ordinary or imperfectly amalgamated zinc is used.

In other words, it is not a mere question as to what is present in a solution; the *compatibility* of the various substances must also be considered, and of this we know very little at present. Incompatible molecules may get in the way and hinder change, but only compatible molecules can co-operate in changes, so that we cannot simply write $C = \frac{E}{R}$, and treat R as the resistance of the solution as a whole in which the change takes place; it may often be the resistance of circuits within the solution, the precise nature of which it is difficult, if not impossible, to determine.

It is not only on account of the very different behaviour of different metals towards acid solutions, however, that the discussion of the electromotive efficiency of various combinations is of interest, it is also possessed of a side interest as throwing light on the behaviour of water itself, which is in so many respects peculiar. If it be possible for sulphuric acid molecules, for example, to separate from a solution—to dissociate out—and act separately in the presence of water, without producing any direct effect on the electromotive force of the cell within which the change occurs, the necessary energy being furnished by the liquid, which thereby becomes reduced in temperature, it is clear that the dissociation of *hydrates* is, in a measure, a phenomenon of a peculiar order. It might be supposed that the energy concerned in such changes is the so-called "bound" energy of Helmholtz, but this can hardly be the case, as that which is "bound" when the acid is included within a circuit with lead is apparently "free" when included in a similar circuit containing zinc in place of lead.

In discussing elsewhere the question whether a line cannot be drawn between cases in which interaction will, and those in which it will not, take place between two pure substances, I have pointed out that, although there is little to guide us, it seems not improbable that water has special properties which enable it to act directly, at least in cases in which dissociable composite electrolytes could be at once formed. If this be the criterion adopted, sulphuric anhydride may be expected to combine at once with water without the intervention of any other substance, but not with hydrogen chloride; and alcohol to mix with water without undergoing hydration, just as ammonia and hydrogen chloride mix without combining.

This distinction is made on the assumption that while all liquid systems of the formula xH_2O,ySO_3 are conductors, the compound SO_3HCl, as well as mixtures of its constituents, and also pure mixtures of alcohol and water, are non-conductors. In drawing this conclusion, it is of course assumed that we can generalise from actual observations with liquids as to their ability to co-operate in forming electrolytic circuits. The difficulty which apparently is met with in coupling carbonic oxide may conceivably arise also in the case of liquids; but it does not appear probable that such will be found to be the case, as mixtures of dielectrics, such as water and hydrogen chloride, so readily conduct a current. Of course, also, no such distinction as is above drawn can be made if pure water be slightly dissociated—as some contend it is.

In attempting to discuss these questions, however, we are entering on a field of inquiry in which, at present, we are all but strangers—we are, in fact, dealing with that remarkable class of combinations, the so-called molecular compounds, whose existence it is impossible to deny, difficult though it be to precisely define them. But that they play an all-important part in the course of chemical change, there can hardly be a doubt; and it has long seemed probable to me that, as I have previously suggested, we may eventually recognise in them the mechanism through which the degradation of energy is effected in chemical changes generally.

With regard to the spontaneous occurrence of dissociation in a case such as that of sulphuric acid, it is all-important, probably, to bear in mind that the compound represented by the formula H_2SO_4 will combine both with sulphuric anhydride, on the one hand, and with water on the other, so that a number of systems of the general formula xH_2O,ySO_3 are possible. There is thus an essential difference between sulphuric acid and ammonium chloride, for example, as the latter has no tendency, apparently, to combine with either of its constituent molecules, and, in fact, constitutes a rigid system. It may well be that it is only in cases comparable with that of sulphuric acid that dissociation occurs spontaneously without the intervention of any other substance, such systems being in the condition postulated by Fitzgerald—*i.e.*, so arranged that changes take place within them of their own accord—and being the only ones which can be formed directly from their two proximate constituents without the intervention of any third substance. The fact that liquid water itself almost unquestionably consists of a mixture of complex molecules and of fundamental molecules such as are represented by the formula H_2O must also be taken into account. In short, it would seem that a sulphuric acid water system may be likened to a complex system of springs, and ammonium chloride to a simple spring; whereas the latter can change only in one direction, and must always be in compression or extension, the former may have one part in compression and another in extension, and fluctuating changes may easily go on within it, and, in consequence, energy be gradually frittered away. Such a fluctuating system may be a necessary element in every chemical change.

It is impossible to doubt that, as a means of determining the precise character of the changes which may be going on in a complex system, the determination of the electromotive efficiency of various combinations will prove to be of the greatest importance. As a further illustration of the manner in which we may derive assistance from the introduction of such physical considerations, attention may be directed to the complex changes attending the action of metals on nitric acid, a subject which has long troubled the minds of chemists, and which has always exercised a special fascination over me. There is little, probably no hope, that we shall ever arrive at a satisfactory solution of this complex problem, so long as we regard it from a purely chemical point of view.

The observations of fundamental importance which must be first taken into account in discussing such changes are those of Millon (1842), Russel (1874) and Veley (1891), showing that silver, copper, &c., are not soluble in nitric acid free from nitrous compounds. In my opinion, however, these observations cannot be regarded as proof that nitrous acid is the solvent of the metal; the conclusion to be derived from them, I think, is of a far more interesting character.

Silver has a negative heat of dissolution, the value calculated from the data given by Thomsen being (at 18°):

$$2Ag + 2HNO_3, aq = -51580 \text{ gram-deg. C. units.}$$

This value, however, is reduced to −40700 if the heat of dissolution of silver nitrate be deducted. As the reduction of nitric acid to nitric peroxide ($2HNO_3 - O = N_2O_4, H_2O$), according to Thomsen, involves an expenditure of but 10010 units, the oxidation by *nitric acid* of the hydrogen displaced by silver dissolving in nitric acid would give 68360 − 10010 = 58350 units, which is considerably in excess of the value − 51580, and still more so if the lower value corresponding to the formation of the anhydrous salt be taken. Silver, therefore, should be easily soluble in nitric acid if this acid can act as *depolariser*. A still stronger case may be made out by considering the values for mercury and copper, as the heats of dissolution of those metals, although negative, are considerably lower than that of silver. Such facts appear to leave little room for doubt, and to justify the important conclusion that the nitrous compound is the active depolariser.

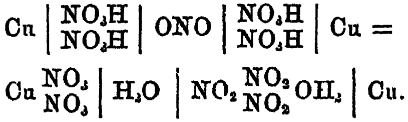
To conclude that such metals as bismuth, copper, mercury and silver are dissolved by nitrous acid, not by nitric acid, is to attribute to nitric acid properties which would make it entirely peculiar among acids, for it appears to be a characteristic property of acids generally to dissolve metals generally whenever the conditions are such that exothermic change can occur.

It seems to me that such problems can only be treated from an electrolytic standpoint, and the fact that we do not always so treat them is evidence of a most extraordinary failure on the part of chemists to apply Faraday's teachings. Unfortunately the physicists have also neglected this subject, having apparently left it to the chemists to discuss the changes attending the interaction of metals and acids; the result is blank ignorance of all that is fundamental with regard to such matters on the part of both chemists and physicists.

Objection has been taken to the use of the hypothesis of nascent hydrogen in explaining the effects produced with nitric acid. No doubt the conception is much misunderstood and misused; but it is, after all, a conception which cannot be put aside. Hydrogen undoubtedly is often displaced and brought into action without ever escaping from the circuit in which, and along which, it is displaced; "nascent" hydrogen, in fact, is but hydrogen in circuit, the hydrogen which is active at the surface of the plates in a Grove's gas battery, or which effects reduction when condensed in charcoal, being as much "nascent" in this sense as that displaced from water, say, by sodium amalgam in presence of a reducible substance. Moreover, the "activity" of such hydrogen depends entirely on its origin. This cannot be denied in face of the fact that if in cells of the Daniell type, for example, cadmium be substituted for zinc, not only is the electromotive force developed lower, but lower to the extent to which the heat of dissolution of cadmium in the acid used is less than that of zinc.

In dissolving metals in nitric acid, we are but dealing with "cells" of the Grove type. If nitrous acid be in any way directly active as solvent of the metal, in all probability it can but act along with the nitric acid, and not to its exclusion; but it is useless to discuss this question further until we are sure that nitrous acid actually exists, and there is much reason to doubt this. As copper is readily dissolved by diluted sulphuric acid in presence of oxygen, although insoluble in the acid alone, it is inconceivable that nitric acid should not be equally active in presence of a sufficiently active depolariser—when the conditions are such, in fact, as are secured by the presence of oxygen together with copper and sulphuric acid, and a system is formed within which exothermic change is possible.

It appears to me to be highly probable that the active depolariser in the cases considered is *nitrogen dioxide*, and that this becomes reduced to nitrogen monoxide, which in turn is oxidised by the nitric acid. Whether these actions all take place in one circuit has yet to be determined, but it is not unlikely that such is the case, as the electromotive efficiency of the Grove cell, as determined by Thomsen, corresponds with the assumption that the nitric acid becomes reduced to nitrogen dioxide ($2NO_2,OH_2$). The dissolution of copper on such a view would be represented as follows :



$$\mathrm{Cu}\left|\begin{matrix}NO_3H\\NO_3H\end{matrix}\right|ONO\left|\begin{matrix}NO_3H\\NO_3H\end{matrix}\right|\mathrm{Cu} =$$

$$\mathrm{Cu}\begin{matrix}NO_3\\NO_3\end{matrix}\Big|\,H_2O\,\Big|\,NO_2\begin{matrix}NO_2\\NO_2\end{matrix}OH_2\Big|\,\mathrm{Cu}.$$

There is thus at once a great increase in the amount of nitrogen dioxide, assuming only a minute proportion to be present in the acid at the outset, and the action can therefore take place at a rapidly increasing rate, and very soon attains a maximum. As soon as the nitric acid is saturated with the dioxide, this begins to escape; but, *pari passu*, the acid grows weaker, and soon the dioxide is subjected to the attack of water, whereby nitrogen monoxide is formed, and also escapes, the acid being too weak to entirely reoxidise it. It is probably from this point onwards that the electromotive force begins to fall. It is conceivable that monoxide is formed even at an earlier stage, in consequence of the exhaustion of the acid at the surface of the plate, and that the electromotive force is also influenced in this manner. In the case of metals having positive heats of dissolution, the phenomena are probably far more complicated, but, as I have pointed out in discussing this question in a note on the nature of depolarisers (Proc., 1893, 148, 188), it is possible, by applying electrochemical considerations, to deduce comparatively simple explanations.

In this note I have also called attention to the case of sulphuric acid as possibly analogous to that of nitric acid, inasmuch as it only undergoes reduction when the conditions are such that the presence of *sulphuric oxide* is possible, *i.e.*, that the active depolariser, when metals such as copper (which have negative heats of dissolution) are dissolved in hot, concentrated, sulphuric acid, is the oxide, not the acid itself. Divers and Shimidzu, in a paper on the action of pyrosulphuric acid on certain metals (Trans., 1885, **47**, 636), have contended that the trioxide acts directly; they formulate the action as occurring between the metal and a double molecule of the oxide, which they represent as sulphuryl sulphate, as in the equation

$$SO_2(SO_4) + 2Ag = Ag_2SO_4 + SO_2;$$

but such an assumption appears to be entirely unnecessary, even if it be in any way warranted by facts.

The fact that metals dissolve in solutions of perchloric acid without reducing it, may be regarded as confirmatory of the view here put forward, as there is no reason to suppose that such solutions contain a reducible oxide; solutions of chloric acid, on the other hand, which undergo reduction by metals, are doubtless comparable with "nitrous" nitric acid.

If it be found that such contentions as these are correct, our views of the manner in which acids act will be much simplified. Whatever view be taken of electrolysis—whether or no it be dependent on the ions becoming free like the molecules of a gas—it is difficult to understand that one compound should function in several different ways in the same circuit. If nitric acid, for example, be resolved into the ions H and NO_3, and these are arranged in any form of polarised chain along the direction in which the current acts, why should the hydrogen which separates from the NO_3 ion, giving place to the metal, act otherwise on a contiguous NO_3 ion than to reproduce nitric acid? A complete "change of front" would be necessary if it were to act in any other way. A company of soldiers who in rigid mechanical obedience to the word of command perforce *face* the enemy to receive their charge, will be bayoneted only in front by those who attack in an equally mechanical manner; if otherwise, the word of command—the directive effect of the E.M.F.—is only partially obeyed. And to say, in order to meet such an objection, that a molecule may undergo ionic disruption in several ways is to entirely confuse our conceptions in a manner which is most undesirable so long as the facts do not *compel* us to make such an assumption.

To explain the formation from chloracetic acid, for example, of salts on the one hand and of hydroxyacetic acid on the other, Ostwald assumes that it not only dissociates into the ions H and $CH_2Cl{\cdot}CO_2$, but also to a slight extent into Cl and $CH_2{\cdot}CO_2H_2$; his theory, in fact, forces him to assume that an electrolyte may ultimately split up in different directions. But no such difficulty arises in connection with the association theory. According to this, the manner in which change will occur depends on the nature of the substances present and the extent to which they are compatible—a compound, such as chloracetic acid, behaving as an acid when substances are present to which the acid radicle is attractive, as a chloro-derivative when substances are present which are more attracted by the chlorine, "local" circuits being established which proceed from and include one or the other part of the molecule, according to circumstances. As the changes which take place when such circuits are established will depend on the nature of the circuits, it is easy to understand the formation from chloracetic acid, on the one hand of hydroxyacetic acid, and on the other of dichloracetic acid, even supposing the chlorine to be the attracting element: the difference would depend primarily on the association with the chlorine atom either of an alkali or of chlorine—*i.e.*, on the difference in the associate. To account for the formation of dichloracetic acid on the ionic hypothesis, it is necessary to assume that chloracetic acid will ionise not merely in two ways but also in a third, viz., into H and $CHCl{\cdot}CO_2H$. Nay, more, if the argument be extended, in order to account for the formation of chloracetyl chloride, $CH_2Cl{\cdot}COCl$, a fourth possibility must be admitted, viz., into $CH_2Cl{\cdot}CO$ and OH !*

I have dwelt thus fully on these questions as, apart from the interest attaching to such problems, it is all important to establish the exact nature of the changes which attend the dissolution of metals and the precise character and functions of substances which act as depolarisers—our power to utilise chemical change at will as a source of energy depending on the extent to which we comprehend the inner meanings of all such changes. The function of the depolariser is far from appreciated—there being too marked a tendency to regard it merely as an agent whereby polarisation is prevented, the fact being often overlooked that it directly contributes in a very important manner to the energy of the cell, in many cases making changes possible which could not otherwise occur.

In all cases of chemical change energy is ultimately degraded, but in most cases a switchback rather than a simple inclined plane is the graphic analogue of a circuit of chemical change. Or, still better, we may liken it to a system of pipes laid up and down hill through which water is supplied to a town, in which case the function of the depolariser is comparable with that of the stand pipe or accumulator at the pumping station, up and through which the water is forced in order to secure the head which is necessary to overcome the friction in the pipes and to cause water to mount the hills in the district supplied as well as to raise it to the tops of the houses and in the fire mains. Such hydraulic systems can only be constructed of pipes which can be fitted together, just as chemical changes can only be brought about between compatible substances. Lastly, those who enjoy a constant service have no right to assume that the supply of water is automatic; on the contrary, a complex organisation which may altogether escape notice is required to secure it. And so it may be in the case of electrolysis and chemical change.

Before concluding this section it is desirable to refer to the behaviour of electrolytes which yield a variety of products according to the conditions under which their electrolysis is effected. For example, that of sulphuric acid solutions which afford not only oxygen and hydrogen, but also persulphuric acid, hydrogen peroxide and ozone. If action take place primarily in an electrolytic circuit in but one way, how are we to account for the formation of persulphuric acid? Its production would appear to afford evidence that the acid acts both as electrolyte and as "oxygen depolariser," which is against the conclusion previously arrived at The difficulty disappears if it be supposed that the first products of electrolysis are hydrogen and persulphuric acid, *i.e.*, that instead of water being directly resolved into 2H and O, or the acid into H and HSO_4, or 2H and SO_4—the conventional views—the acid is converted into 2H and $H_2S_2O_8$. Richarz some time ago advocated this view (*Zeit. physikal. Chem.*, 1889, 4, 28), and it is also in accordance with Ostwald's contention that the dissociation of dibasic acids of the form H_2R'' primarily takes place (in relatively concentrated solutions) into $H + HR''$. It may be supposed that under ordinary conditions, when the electrode surface is large, the decomposition of the persulphuric acid is determined by the tendency of the electrode to attract oxygen; whilst, if the electrode surface be small and the current density high, much persulphuric acid has the opportunity of escaping into the solution, and of remaining to a considerable extent unchanged if the acid at the electrode be more or less concentrated and favour its survival, but somewhat rapidly undergoing hydrolysis into sulphuric acid and hydrogen peroxide in weak solutions. The formation of ozone may in like manner be regarded as the outcome of oxygen depolarisation by the persulphuric acid, *i.e.*, of the interaction of oxygen on the electrode with the acid under the special conditions which attend high current density—or it may be that ozone, not oxygen, is the ordinary product, and that this in turn suffers decomposition at the electrode surface when this is large. It is desirable to lay emphasis on this explanation as at least a possible partial explanation of the extraordinary character of the curve representing the change in conductivity of sulphuric acid solutions on dilution.

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* Why, it may be asked, should the atoms keep together at all, if they are thus willing to separate in so many ways?

It is commonly assumed that we know what happens when a solution of hydrogen chloride is electrolysed: that, in fact, it is directly resolved into hydrogen and chlorine; indeed the primary article of faith in the creed of the ionic dissociationist carries us even further, asserting, as it does, that the chloride spontaneously breaks up into hydrogen and chlorine ions, and that these, giving up their charges at the electrodes, form hydrogen and chlorine molecules. The production of chlorine may, however, be the outcome of secondary changes. Assuming that muriatic *acid* consists of hydrated molecules, let us suppose, of the composition $H_2O{\cdot}ClH$, these may yield a peroxide, $H_2O_2{\cdot}(ClH)_2$, which, in concentrated solutions, either breaks up into chlorine and water, or is so resolved under the influence of the acid, but in weak solutions undergoes hydrolysis, oxygen being evolved by the decomposition of hydrogen peroxide at the electrode surface. Or it may be that the chlorine is oxidised, and a chlorous compound formed from the acid, from which chlorine and water are then liberated by the action of hydrogen chloride.

There is reason to think also that the electrolysis of organic acids may, in like manner, involve initially the formation of "peroxidised" products.

All these are questions which require further experimental investigation and consideration. Meanwhile, it is all important to bear in mind how little we really know of such matters. They fall into the same category as the inquiry into the constitution of acids generally, which, I venture to think, must be regarded as still open to discussion, for in scientific work, as in ordinary life, we are much subject to the influence of waves of fashion, and are even apt to be misled by the beauty of a new conception. Faraday taught that the water was decomposed on electrolysing diluted sulphuric acid, and formerly chemists believed that when a metal dissolved in an acid solution it displaced hydrogen from water, and that the oxide thus formed combined with the acid. The binary theory of electrolysis introduced by Daniell, in 1839 (*Phil. Trans.*, 1839, 97), however, shook faith in this interpretation; but this theory did not gain full acceptance until after the publication of Williamson's entrancing views on the nature of salts and his discovery of chlorosulphonic acid, in 1851–53, from which time onwards the old Berzelian system of representing oxy-acids and their salts was fairly generally abandoned. Yet if we now, without prejudice, calmly review the facts, we cannot but admit, I think, that the verdict must still be "not proven." If we, however, in any way return towards the old view, we shall probably have to steer a middle course, and consider that water is not initially active as such, but rather what may be termed combined water. Should a view of this kind ever prevail, especially if it be admitted that in the case of muriatic acid the active substance is a hydrate, $(H_2O)_x(ClH)_y$, the insight and prescience displayed by the older workers, whose minds were untrammelled by the weight of theory, will deserve fuller recognition than is now accorded to them, and Lavoisier's choice of the name oxygen will be more absolutely justified than it has ever been admitted to be since Davy's investigation of chlorine.

The discovery of the nature of the phenomena underlying electrolysis—and therefore those underlying chemical change—may not improbably be assisted by the study of substances other than conducting solutions: and for other reasons also the study of the electrical properties of such substances appears to be of the highest importance.

Thus it is well known that whereas metals generally are relatively good conductors, non-metals oppose a very great resistance to the passage of an electric current. A question of the utmost importance to consider is whether non-metals may not be capable of opposing an infinite resistance, and whether it may not be possible to base on electrical behaviour an absolute distinction between metals and non-metals, although hitherto we have been obliged, on general chemical grounds, to conclude that no line can be drawn, and that, in fact, the metals insensibly shade off into non-metals through the metalloids* such as arsenic, tellurium, &c.

As long ago as 1887, in the course of the discussions which took place within the Brit. Assoc. Electrolysis Committee, I drew attention to the importance of making further observations on the specific resistances of the non-metals—pointing out that as these appeared all to behave as electrolytes of very high resistance, it became a question whether this might not arise from the fact that impure substances had been studied, and adding "if sulphur, &c., are found to behave as water, that is, to increase in resistance as they more nearly attain a pure state, then I think we may fairly divide elements into two distinct classes, and define a metal as an element which conducts, and a non-metal as an element which insulates."

The behaviour of sulphur, selenium and other well-defined non-metals, in fact, is such, that there is hope, I think, that eventually we may be able to draw such a distinction. It is true that Monckmann in 1888, in a paper communicated to the Royal Society on the specific resistance, &c., of molten sulphur, showed that this substance had a not inconsiderable conducting power; and that when objection was raised against the results on the ground that no special care had been taken to purify the sulphur, he extended his experiments, recognising the necessity of obtaining "the purest possible specimens of sulphur," but arrived at results essentially in agreement with his earlier observations. Apart, however, from the fact that the methods of purification he adopted can scarcely be regarded as calculated to afford a "pure"† material, and that there is internal evidence in the paper that he was not dealing with a pure substance (it can scarcely be doubted that "pure" molten sulphur would be without action on platinum), it may be noted that only about six months intervened between the presentation of his two papers; had six years been devoted to the task, the conclusion arrived at might, perhaps, have merited confidence.

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* Nothing more clearly shows how careless we are in our use of language, and insensible of the meanings of words, than the conventional use of metalloid as the antithesis of metal.

† It is time that we ceased to speak of substances as *pure*, as a pure substance is and must ever remain an ideal conception; and while there can be an infinite number of degrees of impurity, there can be none of purity. The much misused

In point of fact, it is necessary that the lessons taught by work such as that done by Stas should be seriously taken into consideration, and that the extraordinary experimental difficulties which such problems present should be more generally recognised. The almost child-like simplicity of faith and belief in the chemists' ability to purify which distinguish our physical colleagues is most remarkable. If we even venture to point out that the material which has been measured with such infinite pains may have scarcely merited so much attention, and thereby hint that the results therefore, perhaps, are but of slight absolute value, we are at once told, "Oh, if you will give us pure stuff, we will examine it"; and they might add—but do not—"and secure the credit which will ultimately attach to the work," inasmuch as the mass of figures which they put forward impress the public, whilst the modest statement made by the chemist of the precautions which he has taken in purifying the material—work which may well require the expenditure of infinitely more knowledge and experience, thought, time and labour than the physical measurements—cannot be appreciated by those who have not themselves taken part in such work. During the past twenty years, Fellows of our Society have contributed in a remarkable manner to our knowledge of physical constants, and their work will have an abiding value, as they have taken very special precautions in selecting and purifying the substances examined; but hitherto there has been absolutely no reciprocity, physicists having remained con-

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phrase, "chemically pure," has no abstract meaning and should be discarded; it is usually nothing more than a convenient fiction, made use of by sellers of chemicals. Thus, the presence of arsenic in zinc being objectionable because zinc is used in testing for arsenic, it became customary to sell zinc freed as far as possible from arsenic as chemically pure, although other impurities were often present in such zinc in considerable quantities. Purified should be substituted for pure.

Chemists are sufficiently serious offenders, but others also are not infrequently guilty of like thoughtlessness, as, for instance, when a paper headed ". . . properties of *pure* iron" is prefaced with an analysis showing the presence in the "*almost pure* iron" of small amounts of carbon, sulphur, silicon, and manganese in what is first spoken of as a sample of *very pure* iron. Or when, again, it is stated that "the yield will of course depend on the *amount of purity* required. From . . . . about one-tenth of *quite pure* . . . . can be obtained, and about one-twentieth of *very pure*." Language may, indeed, be said to be an instrument for the concealment of thought when these abuses of it are possible. Surely, if devoted to science, we should be scientific in all things!

tent with a knowledge of the very first principles of chemistry. In the future there must be more effective co-operation between us. In making these remarks, I do not wish to blame physicists entirely. I hold that we are ourselves largely responsible for such a condition of affairs, and that it is in no slight measure due to the unscientific manner in which our subject is taught, and especially to the manner in which it is overlain with details which obscure the logical interconnection of its parts.

To return to sulphur, an abstract account has recently been published in the Proceedings of the Royal Society (1894, **56**, 32) of observations by Threlfall, Brearley and Allen, on the electrical properties of *pure* (*sic*) sulphur, *i.e.*, sulphur from the Chance recovery process purified by distillation and exhaustion *in vacuo*. Such a process cannot be accepted as by any means an exhaustive one, and it appears almost to be a case of "love's labour lost" to apply to such material the infinite care which the authors appear to have taken in making the electrical measurements. Yet they arrive at the important conclusion that so long as a single modification be dealt with, such sulphur does not conduct while solid. A mixture of two modifications, however, does; but in view of the possibility of changes taking place during the production of the mixture—of conducting impurities being introduced or generated, it is difficult to regard this latter conclusion as established, the more so as the authors in question have found that as the temperature was raised, the conductivity of the sulphur increased slightly up to the melting point, when there was an enormous increase.

Passing to selenium, there can be little doubt that the properties attributed to this element, and especially its extraordinary behaviour on exposure to light, have been deduced from observations with very impure materials. Shelford Bidwell's recent account of his investigation of this element is full of interesting observations showing, as he says, that the conductivity of crystalline selenium appears to depend principally on the impurities which it contains in the form of metallic selenides (*Phil. Mag*, 1895, [5], **40**, 233).

The conductivity of what is so wrongly called carbon, in the form used for electric light purposes, is well known to be also electrolytic in character, and is, therefore, most probably conditioned by the presence of salts, and not a specific property of the modification of the element present in such materials.

In the case of the metals also, on the other hand, many observations of great interest have been made, which are highly suggestive, and should serve to incite further inquiry.

The electrical conductivity and, at the same time, the mechanical properties of all the highly conducting metals which fall into positions in the periodic system not far removed from that of copper are affected in a most remarkable manner by the presence of minute amounts of impurity, especially by certain non-metallic and metalloïdal impurities. Owing to the very large use which is made of it in telegraphy, no metal has had more attention paid to it than copper, its manufacture having been greatly improved by the introduction of electrolytic methods in place of the old dry methods. Fitzpatrick, in a report on the specific resistance of this metal, published in the *Brit. Assoc. Report* for 1890, gives a value which is better than that found nearly 30 years before by Matthiessen for "pure" copper in the proportion of 100 : 102·6; but my colleague, Professor Ayrton, tells me that copper of still higher quality, viz., above 103, is now made on a large scale. It is noteworthy that Swan and Rhodin, in a paper communicated to the Royal Society in 1894 (**56**, 64), give a value which is not quite so low as that found by Fitzpatrick, viz., 1563, Fitzpatrick's lowest value being 1557. They speak of their copper as "pure," stating that it is probable that both of the specimens examined by them were "perfectly pure," and that, in fact, the limit of electrolytic purification had been reached; but this cannot have been the case. Moreover they, as well as Fitzpatrick and all other observers, obtained different values before and after annealing, the specific resistance of the soft wire being 1563 whilst before annealing it was 1603—a circumstance which, in itself, I venture to think, affords strong presumptive evidence against the conclusion that we are yet come into possession of practically pure copper, and for the following reasons.

E. van Aubel has observed in the case of bismuth (*Phil. Mag.*, 1889, **28**, 332), that although annealing has a considerable effect when the metal is very impure, the effect becomes less and less marked as the impurities are removed, until finally the electrical resistance is scarcely altered by annealing; also there is a considerably greater difference apparent between the values given for hard and soft copper by Matthiessen than has been found by later workers, who, presumably, have dealt with a less impure metal. Therefore it appears not improbable that a pure material would suffer no change on annealing—that it would not require annealing, in fact.

Taking Spring's important investigation into the influence of extreme pressure into account, it appears likely that the change during wire drawing—hardening, to undo which resort is had to annealing—is in itself due to the occurrence of chemical change, that is, change in molecular composition; Barus, in particular, has advocated this view (compare *Nature*, 1890, **41**, 369), and it has recently received confirmation from observations made by Unwin on the effect of repeated straining and annealing on the yield points of iron and steel

(*Proc. Roy. Soc.*, 1894, **57**, 178). But, if change in molecular state in a metal be subject to the same laws as are interactions in other cases, a pure material should not undergo change under the influence either of pressure or of heat; and, therefore, from this point of view also the fact that all copper hitherto examined is softened by annealing may be regarded as evidence that it has contained impurity.

The nature of the "impurity," the character of the changes which take place in such cases, form subjects of inquiry not only interesting in themselves, but also of the highest technical importance. With regard to the former, attention may be called to a statement made by Hartley to the Brit. Assoc. Electrolysis Committee in 1887, pointing out that the preparation of pure copper is extremely difficult; and that such as he had had made for spectroscopic purposes, which was considered *pure*, had been found to contain as sole impurity about one hundred thousandth part of silver, while other samples contained tellurium and bismuth. The photographed spectra were the means of detecting these foreign constituents. I quote this by way of reminder that ordinary or even extraordinary chemical tests are of no use in such cases. It must also not be forgotten that gases may become "occluded" during annealing, and, bearing in mind the extreme sensitiveness of copper—especially to oxygen—it would appear necessary in future inquiries to effect the annealing in a "vacuum" from which moisture, oxygen, &c., have been, as far as possible, removed.

As regards the character of the changes brought about in metals by admixture, we are, of course, but on the very fringe of the inquiry; it is certainly cause for congratulation that men like Roberts-Austen, Dewar (and Fleming), Heycock and Neville, and Alder Wright—all our own Fellows—have done so much during recent years to extend our knowledge of the behaviour of metals; and we may confidently expect that, now interest is so generally re-awakened in metals and alloys, we shall ere long be able to arrive at trustworthy conclusions.

Recent observations on the depression of the freezing points of metals seem to show that, in most cases, the liquid metal consists of monatomic molecules—in itself a very noteworthy conclusion, when it is remembered that the very opposite is true of liquefied non-metals. Whether on solidification, and as cooling takes place, these fundamental molecules form complex groups, is a question which is now being warmly debated, but is a very difficult one to decide: the view advocated by Matthiessen—I am inclined to think with true prescience—that many metals are capable of existing in allotropic modifications, that is to say, in modern language, that they may exist of different degrees of molecular complexity, is at the present time but little approved of, there being a tendency to substitute for it more purely mechanical conceptions. Only in the case of iron is it fairly generally admitted that the facts are such as to make the acceptance of Matthiessen's view almost compulsory. Osmond—whose work is of extraordinary interest and of the highest value—indeed has argued that this metal may exist in no fewer than three allotropic forms.

In the case of a pure metal consisting in the fused state of monatomic molecules, it is conceivable that when solidification takes place interatomic forces come into action in such a manner and so uniformly that the mass, as it were, forms one huge complex molecule. This could scarcely happen if impurities were present; but in that case similarly constituted smaller complexes—individual crystals—might form. The observations of Behrens on the microscopic structure of alloys of silver and copper are perhaps of significance from this point of view, showing as they do that, whilst the crystals are scarcely distinguishable in "pure" copper, in copper containing only a minute proportion of silver they become distinctly visible and are seen to be separated by a film of white alloy.

It is difficult to resist the conclusion that the properties even of congeries of such crystal molecules as are above referred to are not somewhat different from those of the simple fundamental molecules *en masse*. Silver, copper and gold, it is well known, are possessed of high electrical conductivity, especially silver and copper, which are all but alike in this respect; and yet, as Matthiessen has shown, when any two of them are mixed, the conductivity of the mixture is lower to an extraordinary extent than that of either alone. That such an effect should be produced is very remarkable, and it is difficult to understand how it can be brought about by the mere admixture of molecules which apparently are equally effective conductors; this behaviour would seem, indeed, to be an indication either that the molecular state of the metal is changed, and that, in fact, it is converted into a modification possessed of lower conductivity; or that a compound of the two metals of lower conductivity is formed and becomes interposed between the highly conducting crystals.*

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* In view of the possibility that impurities introduced during the preparation of such alloys may exercise an important influence, it is very desirable that Matthiessen's observations should be repeated and extended, using very carefully purified materials. No doubt the greatest care has been taken in purifying both gold and silver, as well as copper, but there is no reason to think, I imagine, that we have attained to finality in such matters. These three metals are so much alike in many of their properties that it is an interesting subject for inquiry whether they may not be still more closely allied, especially in electrical behaviour, than we now suppose them to be, and it is very desirable that they should all be worked at from this point of view. In future, however, it will be necessary to extend the examina-

The remarkable behaviour of silver towards oxygen also serves to suggest that the silver atoms combine on solidification. The fact that this metal is a solvent specifically of oxygen, and not of gases generally, is, in a measure, evidence that combination takes place between it and the gas; and on this assumption the well-known spitting may be explained as due to the occurrence of an interaction conditioned by the superior affinity of silver to silver outweighing that of silver to oxygen in the manner indicated by such an equation as $x\mathrm{AgO}_2 = \mathrm{Ag}_x + x\mathrm{O}_2$. But this explanation does not necessitate the conclusion that the silver atoms combine otherwise than throughout the whole mass.

The evidence that one metal may combine with another is now so entirely beyond question that it is no longer open to doubt that like metallic atoms may combine. The eminently plastic character of some highly purified metals, *e.g.*, copper, gold, silver, iron, platinum—would, I imagine, lead us to prefer the view that they consist of relatively simple, if not of monatomic molecules. Whilst, on the other hand, the extraordinary brittleness produced on adding small proportions of certain elements to some of these metals is perhaps best explained by the assumption that such additions cause the formation of complex molecules having but little tendency to cohere. Such a conclusion is almost necessary in the case of iron, in which, as is well known, extraordinary alterations may be produced by altering the distribution of the impurities, without altering their amount—I allude to the passage of carbon from the combined into the free state during the rapid cooling of steel, and to the change in the opposite direction which takes place during slow cooling. Iron, indeed, is one of the most remarkable among metals, and there is no literature more deserving of the chemist's attention than that relating to the researches of Roberts-Austen, Barus, Hopkinson, Osmond and others who, during recent years, have contributed in a most important manner to our knowledge of the changes going on in iron and steel.

Osmond assumes that even "pure" iron alters in molecular com-

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tion so as to determine as many properties as possible, mechanical, physical and structural. If we knew, for example, the specific conductivities, as well as the tensile strength and extensibility, of the various gold alloys prepared by Roberts-Austen (*Phil. Trans.*, 1888, **179**, 339), we should be better able to discuss his conclusion that the influence of various metals on the mechanical properties of gold may be co-ordinated with their atomic volumes—a conclusion which it is somewhat difficult to accept when lithium and potassium produce effects which place them at the very opposite ends of the scale. The improvement effected in metals and alloys by the addition of another—as that of aluminium to brass—may doubtless sometimes be traced to the fact that it brings about the removal of an objectionable impurity, and this may well be the effect on gold of some metals.

position as it cools, basing this conclusion on the observation that the electro-deposited metal exhibited the phenomenon of recalescence —but the conclusion that such iron is, to use Roberts-Austen's expression, "as pure as any iron can be" may fairly be called in question, especially as Osmond speaks of it as containing a little carbon (0·08 per cent., *Iron and Steel Institute*, 1890, i, 38), and it may be doubted whether any such change would take place in pure iron. In presence of carbon, it would seem that when the temperature has fallen sufficiently molecules which are more complex than those existing at the higher temperature are formed, heat being liberated, thus giving rise to recalescence; the extent to which such complexes are formed largely depending on the amount and character of the impurity present. Perhaps it is from these complex molecules that the peculiar magnetic properties of steel are derived. The separation of carbon from iron may well take place at the moment when the complexes are formed, and the change which occurs at its separation may be of the character of that referred to above in connection with the spitting of silver. The carbide which is produced during slow cooling may conceivably be generated by the interaction of the complex molecular form of iron with the carbon. The explanation of the changes here discussed, advanced by Osmond, involving as it does the assumption that at high temperatures iron consists of the hard modification which unless prevented passes into the soft modification on cooling, seems to me to be less natural and likely than the foregoing.

It is to be hoped that ere long methods will be devised of preparing considerable quantities of iron in a state closely approaching to that of purity, so that the individual influence of various foreign substances may be studied. At present we do not seem to be aware whether the presence of carbon especially is essential to hardening, and whether this element alone can condition the state which renders steel capable of becoming permanently magnetic. Sufficient will have been said, I trust, to emphasise the extraordinary importance of attention being paid to the behaviour of highly purified substances. Enough is known to warrant the assumption that in many cases such investigations will show that properties associated with individual substances are wrongly regarded as specific, and that in reality they are determined by an admixture. To give but one more illustration, if conduction in solids other than metals be always electrolytic conduction, conditioned by the presence of composite electrolytes, a condenser such as a Leyden-jar may be regarded as a voltaic cell in which the electrolyte is a solid of high resistance, and its action as dependent on polarisation; the difference between such a cell and one containing a fluid electrolyte, arising from the fact that in the latter polarisation cannot be maintained except at the electrodes, whilst in the former the polarisation extends throughout the electrolyte. On this assumption it should be impossible to form a condenser from a pure substance. I venture to point this out as showing the great importance of experiments being instituted with very highly purified dielectrics.

The more our attention is directed to the important part which impurities play in determining change, whether it be in metals, non-metals or compounds, the more necessary is it to inquire into the possible mechanism by which such change is brought about. So long as we are entirely unaware of the nature of chemical affinity and of the manner in which it is exerted, little progress can be made; there can scarcely be a doubt, however, that what has been termed residual affinity is largely operative, as, indeed, Faraday foresaw. The following remarkable passage in his fifth series of researches (§ 523) is almost as clear a statement of this view as could be given at the present day.

> "The theory which I have ventured to put forth (almost) requires an admission that in a compound body capable of electro-chemical decomposition the elementary particles have a mutual relation to, and influence upon, each other, extending beyond those with which they are immediately combined. Thus, in water, a particle of hydrogen in combination with oxygen is considered as not altogether indifferent to other particles of oxygen, although they are combined with other particles of hydrogen; but to have an affinity of attraction towards them, which, though it does not at all approach in force, under ordinary circumstances, to that by which it is combined with its own particle, can, under the electric influence, exerted in a definite direction, be made even to surpass it. This general relation of particles already in combination to other particles with which they are not combined is sufficiently distinct in numerous results of a purely chemical character . . . . and it probably has a direct relation to, and connection with, attraction of aggregation both in solids and fluids. It is a remarkable circumstance that in gases and vapours, where the attraction of aggregation ceases, there likewise the decomposing powers of electricity apparently cease, and there also the chemical action of quantity is no longer evident. It seems not unlikely that the inability to suffer decomposition in these cases may be dependent upon the absence of that mutual attractive relation of the particles which is the cause of aggregation."

Hence, in studying the manner in which chemical change is brought about, we are necessarily obliged to consider valency, comprehending under this term both the quantity and the quality of the "affinity" possessed by atoms. But, again, progress is trammelled by tradition and fashion—the habit of teaching dogmatically has affected our whole attitude towards such questions, our theories being not only unsatisfactory, but eminently narrow in their disregard of facts, especially apparent in our neglect of molecular compounds. Helmholtz, in his Faraday lecture, after dwelling on the conclusion that definite atomic charges of electricity are associated with the atoms of matter, said that he did not suppose that the existence of other molecular forces, working directly from atom to atom, was to be excluded. But is this the case? I venture to think that, had Helmholtz been a chemist, he would have felt compelled to admit that whatever be the nature of chemical affinity, the same forces are active throughout—that what is termed residual affinity is of the nature of ordinary affinity, and that the difference is in quantity rather than quality. To repeat what I said in 1888 in a note on valency especially as defined by Helmholtz (*Phil. Mag.*, 1888, [5], **25**, 21), I do not hesitate to affirm that, from the chemical point of view, it is impossible to adopt the Helmholtz explanation of valency unless physicists are prepared to grant the possibility of the "division" of the unit charge. In the paper in question, to explain my meaning, I developed what may be termed a skewer hypothesis of valency, desiring to give a graphic expression of chemical facts and thus help those who are not chemists to appreciate our position. Representing unit valency or charge by a single line, I postulated this line as capable of passing through the atom, and the atom as moving with more or less of freedom on the line. The union of two atoms was pictured as an overlapping of the unit lines. On this hypothesis, in cases in which the atoms do not move out to the end of their lines on combining, free ends would exist, by the overlapping of which combination between molecules could be brought about; and if it be supposed that hydrogen and the metals alone move freely on their lines, in order to give expression to the peculiar differences which apparently are manifest on contrasting the two classes of elements, the combination of a non-metal with a metal may be represented as involving the motion of the former alone out to the end of its line, leaving the line of the non-metal with a free end. In this manner expression may be given to what appears to be a fact, namely, that the non-metals condition the formation of molecular compounds.

What may be termed the *proper valency* of an atom—the number of atomic charges carried by, or of unit lines passing through, the atom—on this hypothesis, is a function of the atom alone, whilst its *residual valency* in a compound is a complex function depending also on the atoms with which it is in association. This is well illustrated in the case of nitrogen by the behaviour of the amines—in all of which the nitrogen clearly functions as a triad—towards haloïds and acids, the extent to which basic characters are manifest depending in an extraordinary degree on the nature of the radicles associated with the nitrogen atom. Assuming that the proper valency of nitrogen is three, the formation of ammonium compounds from amines may be represented as due to the overlapping of the free end of the halogen line and that of one of the nitrogen lines; and if, in a case like that of the chloranilines, it be supposed that the effect of weighting the C_6H_5 radicle by introducing chlorine is to reduce the amount of free end of the nitrogen line to which it is attached, expression is given to the fact that the amine becomes less and less basic, and more particularly that the salt becomes less and less stable as each fresh atom of chlorine is introduced, length of overlap being regarded as the measure of affinity.

It may be asked why, on this hypothesis, if the nitrogen atom carries three atomic charges—is penetrated by three lines—it does not combine with three molecules of acid. Of course, at present no definite answer can be given, but, bearing in mind that the conviction is becoming more and more clearly established that affinity has direction and that geometrical considerations come into play, it is at least conceivable that the direction of two of the lines is such that their free ends perhaps meet, or that they are so directed towards each other that other lines are prevented from overlapping them. The introduction of some such conception would seem to be necessary to explain the remarkable behaviour of compounds such as nitrous oxide and diazoimide, N_3H, the inertness of which is most surprising, whatever view be taken of their constitution. Certainly, the difference between "unsaturated" nitrogen and "unsaturated" carbon which is manifest on contrasting these compounds with the olefines is most remarkable.

But it cannot be denied that, however possible it may be to "explain" the ammonium compounds on the assumption that nitrogen is but a triad, there are cases in which it is difficult to apply any such hypothesis as the above—one of the most striking being that afforded by the remarkable phenyliodonium compounds described by Hartmann and V. Meyer. It will scarcely be doubted by anyone, I imagine, that these and the equally remarkable iodoso-derivatives are not all to be regarded as proof that iodine is not merely a monad, but also a triad element—and yet it must not be forgotten that an iodine atom can combine with but a single hydrogen atom or methyl group, and that hydrogen and methyl are as yet the only trustworthy and, so to speak, legal standards by which the proper valency of an element can be measured. Even in such a case, therefore, a formula similar to that given to the ammonium compounds, viz., $C_6H_5 \cdot I \cdot I \cdot C_6H_5$, cannot be put aside as absolutely out of the question; and if we bear in mind the peculiar character of the oxy-acids derived from the halogens, it is clear that much remains to be learnt of these elements. These acids are often quoted as arguments in favour of the view that the halogens are polyad elements, Mendeléeff having carried his poetic generalisations so far as to claim heptadicity for them; but even assuming that an oxide Cl_2O_7 exists, so long as we are unaware of its structure, we must remain unable to judge of the valency of its elements; we are certainly as little justified in assuming that it contains heptad chlorine as we should be in concluding from the existence of a compound of the formula C_6H_6 that carbon is a monad: valency is far too complex a function to be determined by a simple division method. It is not improbable that the oxy-acids in question are cycloïds.

The solubility of a substance such as triethylphenylammonium iodide in water, in which the amine and haloid from which it is derived are so slightly soluble—and the fact that in the case of the ammonium salts of the chlorinated anilines above referred to hydrolysis of the salt takes place with increasing facility as the amine becomes less basic—may be referred to in further illustration of the difficulties to be overcome in formulating a consistent and sufficiently comprehensive theory of valency. On the hypothesis that such compounds are formed by the overlapping of the free ends of the lines of affinity, the compound should remain saturated or externally inactive so long as there was any overlap; on the other hand, if the somewhat more elastic atomic charge hypothesis be adopted, and it be supposed that any portion of the charge remaining unneutralised might be active, at least the case of the chloranilines would meet with an explanation.

But all these are matters of pure speculation, and I should not venture to allude to them, did I not feel that it is essential that now the amount of material at our disposal for discussion is so very large, it is time that some attempt were made to arrange it in such a form that the results won by chemists can be laid open to inspection by physicists and others capable of taking such transcendental questions into consideration. The theory of types and its logical outcome—the theory of bonds have contributed in a remarkable manner to the progress of our science; and to these geometrical conceptions have now been added which are leading to further important developments—but it can only be supposed that such theories will all prove eventually to be of provisional value, and that far less mechanical conceptions must prevail.

Underlying all modern chemical inquiries there is an obvious desire to determine the structure of molecules generally, as well as to correlate structure with function; and most important advances in these directions have already been made. Whatever view we may hold, it is only too clear, however, that the conventional treatment of the subject involves the disregard of much that is of the highest importance; especially is it, perhaps, too commonly forgotten that whilst the determination of valency involves the knowledge of the structure of the compounds of elements whose valency is sought, the determination of structure is itself based on an assumed knowledge of valency. We are not only being led to frame the conception that affinity has direction, but also that its strength largely depends on the direction in which it is exercised (as shown by the very different behaviour and stability of cycloïds of different dimensions), and it is more than probable, therefore, that ere long we may formulate a theory in which the somewhat mechanical bonds to which we have become accustomed will give place to a more comprehensive hypothesis.

Faraday, in the paragraph previously quoted, regards both the hydrogen and oxygen in water as possessed of "residual affinity," and in his day, no doubt, there was no reason to draw any marked distinction between the two classes of elements—the metallic and non-metallic. But there is much in the behaviour of the latter which seems to me suggestive of the conclusion that they are the mainly active, attracting elements, and those in fact which condition chemical change; I venture to think that this will more generally be admitted to be the case than it is at present, when the facts are carefully considered. We have, it is true, long since abandoned the idea that only elements of opposite classes have considerable affinity for each other, but we are not yet advanced much beyond this, and have yet to recognise that the non-metals have very special mutual affinities.

It is in the play of these affinities more particularly that I am inclined to seek that conjoint influence to which I have frequently adverted by which electrolysis, and therefore change is, it seems to me, brought about. The force of the objection made to this explanation that there are no appreciable reverse electromotive forces within an electrolyte may easily be overestimated. Adverting to what was said above with reference to the phenomena involved in charging a condenser, if any similar effect were produced in a fluid electrolyte if any internal polarisation were set up—it would at once be discharged; and such polarisation would be imperceptible, just as in the case of the determination of conductivity by an alternating current method. A considerable amount of work might, therefore, be done by the current unperceived, and the forces might well be enormous even within the liquid (compare Lodge, *Brit. Assoc. Report*, 1890, 330). I am loth to believe also that the low values found for "ionic velocities" are in truth the velocities of the ions, and would prefer to regard them as but differences between values of which at present we have no conception.

A similar argument will apply in the case of osmotic pressure phenomena, and therefore generally in explanation of the regularities observed in the case of dilute solutions. To say that the osmotic pressure is due to the dissolved substance alone, appears to me to be but a useful figure of speech—in reality, the phenomena must be due to both solvent and dissolved substance. Although one attracts the other, however, the unions are probably but temporary, and the opportunities given for exchanges to take place are so infinitely numerous that the dissolved substance behaves practically as an almost perfect gas. From this point of view it is also not remarkable even that the pressure should have the same value as it would have if the substance were gasified, for, inasmuch as the molecules of the dissolved substance are kept apart by those of the solvent, they are practically in the gaseous condition.

As regards the superior effects produced by electrolytes, I would repeat what I said at Leeds in 1890 (*Brit. Assoc. Report*, p. 326), that, having been able by observations of electrical conductivity as well as by other methods to classify electrolytes in the order of their activity, we are now in a position to apply the correction required to discount the superior effects produced by such compounds in comparison with dielectrics. Why they are specially active, the future must decide. To me it seems that their activity is attributable to their special composition and structure—particularly to the presence in them of either oxygen or halogen in an eminently unsaturated condition, and possessed, therefore, of considerable residual affinity.

As regards semi-permeable membranes, as they have been called, I imagine we have yet much to learn in explanation of these. That the membranes through which liquid diffusion takes place cannot be mere sieves, there is hardly a doubt, otherwise it would scarcely happen that gases only diffuse through septa consisting of materials in which they are soluble: as illustrated by the diffusion of oxygen through caoutchouc and silver, of carbonic oxide through iron, and of hydrogen through platinum and palladium.

In the case of colloïd membranes, through which so many crystalloïds pass, everything seems to depend on the peculiar relationship of water to such matters—a relationship which is so apparent in many physiological phenomena—and at the same time of water to crystalloïds.

The foregoing may be said to be an essay in advocacy of a theory of *association* in explanation of chemical change, as opposed to one of *dissociation*. The attempt has been made to show that such a theory is of universal application, whilst the dissociation hypothesis is apparently not only of limited application, but in some cases irreconcilable with the facts. It also involves assumptions which it is difficult for the chemist to grant: I allude particularly to the main article of faith in the dissociationists' creed that a certain very limited class of compounds—electrolytes—fall to pieces, as it were, more or less completely on entering into solution. As I have implied over and over again, such an assumption necessitates a profound distinction being made between electrolytes and other compound molecules generally which is not patent to the unprejudiced observer, and for which no motive or reason whatever can be assigned. It must not be forgotten that Clerk Maxwell was led by reasons of this very kind to remark that chemical combination is a process of a higher order of complexity than any purely electrical phenomenon.

I have sought also to make clear the great importance of the part played by "impurity" in Nature in conditioning chemical change—a part which seems to meet with an explanation from the association but not from the opposite point of view. The influence of impurities on properties has also been specially noted.

Lastly, the insight which the study of the electrical behaviour of substances generally promises to throw on almost all of the chief problems of chemistry has been briefly touched on.

I am only too conscious that my discussion of all these questions is not only incomplete, but very general and even vague in many places, language being sometimes used—as in quoting from Faraday—in a sense which may somewhat offend the purist; probably, however, the object I have in view will be clear even in these cases.

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ERRATA.

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Page	Line	
912	18*	*for* "crystallisation" *read* "cupellation."

Vol. LXIII (Trans., 1893).

724	8	,, "R. C. Maclaurin" *read* "J. S. Maclaurin."

Vol. LXV (Trans., 1894).

910	15*	*before* "The properties of" *insert* "The formula for the crystallised acid differs from that of dihydroxytartaric acid by two atoms of hydrogen."

Vol. LXVII (Trans., 1895).

189	2	*for* "*d*" *read* "δ."
215	9	,, "50·39" *read* "59·39."
454	14*	,, "and that the explanations" *read* "and believe that the explanations."
563	21	,, "methylic thiocyanate" *read* "methylthiocarbimide."
564	14	,, "really" *read* "nearly."
845	5*	,, "30·86 – 32·03 | + 0·026," *read* "42·41—44·04 | + 0·036."
865	3*	col. ii, *for* "30·86" *read* "42·41."
,,	2*	,, ,, "30·99" ,, "42·60."
,,	bottom	,, ,, "31·06" ,, "42·69."
866	top	col. i, ,, "31·41" ,, "43·21."
,,	2	,, ,, "31·81" ,, "43·73."
,,	3	,, ,, "32·03" ,, "44·04."
871	4*	*Delete.*
872	8	*after* "increases" *insert* "The values of Q cannot be expressed by any simple equation."
1013	14*	*after* "acid" *insert* "distilling the chloric acid thus obtained."
1014	17*	*for* "$Ag(ClO_4)_2$" *read* "$Hg(ClO_4)_2$."

* From bottom.

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